THE
ANALYST

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dealing with all branches
of Analytical Chemistry:
the Journal of the Society
for Analytical Chemistry

THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ORDINARY MEETING

AN Ordinary Meeting of the Society, organised by the Microchemistry Group, was held at 7 p.m. on Friday, February 7th, 1958, in the meeting room of the Chemical Society, Burlington House, London, W.1.   The Chair was taken by the President, Dr. J. H. Hamence, M.Sc., F.R.I.C.

The following papers were presented and discussed: "Applications of the Conway Diffusion Technique to the Analysis of Radioactive Materials for Trace Impurities," by J. K. Foreman, B.Sc., A.R.I.C.; "The Use of Long Chain Quaternary Amine Salts in the Solvent Extraction of Metal Ions," by R. Powell, A.R.I.C.

NEW MEMBERS

ORDINARY MEMBERS

James Alexander, A.H.-W.C.; Robert B. Carson, B.A., M.Sc. (Wisconsin), F.C.I.C.; George Anthony Davidson, A.M.C.T., A.I.M.; Robert Greenhalgh, B.Sc. (Lond.); Harry Ashworth Main, B.Sc. (Manc.); Lloyd A. McDonald, B.S.; Eric Morris, L.I.M.; Nakaaki Oda, Dr.Tech. (Tokyo); Eric Hodson Paulson, M.Sc. (Manc.); Eric Herbert Brodie Sellwood, B.Pharm. (Lond.), F.P.S., A.R.I.C.; Brian Alan Wills, B.Pharm. (Nottingham), Ph.D. (Lond.), M.P.S., A.R.I.C.

WESTERN SECTION

A JOINT Meeting of the Section with the Cardiff and District Section of the Royal Institute of Chemistry was held at 7 p.m. on Wednesday, December 18th, 1957, at the King's Head Hotel, Newport.   The Chair was taken by the Chairman of the Western Section, Mr. P. J. C. Haywood, B.Sc., F.R.I.C.

A lecture on "Inorganic Chromatography" was given by F. H. Pollard, Ph.D.

MIDLANDS SECTION

AN Ordinary Meeting of the Section was held at 6.30 p.m. on Thursday, January 16th, 1958, in the Mason Theatre, The University, Edmund Street, Birmingham, 3.   The Chair was taken by the Chairman of the Section, Dr. R. Belcher, F.R.I.C., F.Inst.F.

The following paper was presented and discussed: "The Analytical Chemistry of Nitrogen," by A. F. Williams, B.Sc., F.R.I.C.

MICROCHEMISTRY AND PHYSICAL METHODS GROUPS

A JOINT London Discussion Meeting of the Microchemistry and Physical Methods Groups was held at 6.30 p.m. on Wednesday, January 8th, 1958, in the restaurant room of "The Feathers," Tudor Street, London, E.C.4.   The Chair was taken by the Chairman of the Physical Methods Group, Mr. R. A. C. Isbell, A.Inst.P.

A discussion on "Advantages of Spectrophotometric Titrations" was opened by R. A. Chalmers, B.Sc., Ph.D.

MICROCHEMISTRY AND BIOLOGICAL METHODS GROUPS

A JOINT London Discussion Meeting of the Microchemistry and Biological Methods Groups was held at 6.30 p.m. on Wednesday, December 18th, 1957, in the restaurant room of "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Chairman of the Biological Methods Group, Dr. S. K. Kon, F.R.I.C.

An informal discussion on "The Weighing and Measuring of Small Quantities" was opened by G. F. Hodsman, B.Sc., Ph.D., A.Inst.P., and R. Goulden, A.R.I.C.

BIOLOGICAL METHODS GROUP

THE thirteenth Annual General Meeting of the Group was held at 6.30 p.m. on Wednesday, December 18th, 1957, in the restaurant room of "The Feathers," Tudor Street, London, E.C.4, immediately before the joint discussion meeting reported above. The Chair was taken by the Chairman of the Group, Dr. S. K. Kon, F.R.I.C. The following Officers and Committee Members were elected for the forthcoming year:—*Chairman*—Dr. S. K. Kon. *Vice-Chairman*—Dr. J. I. M. Jones. *Hon. Secretary and Treasurer*—Mr. K. L. Smith, Standards Department, Boots Pure Drug Co. Ltd., Nottingham. *Members of Committee*— Miss J. Stephens, Messrs. G. C. Ashton, W. A. Broom, S. A. Price, Magnus Pyke and J. Simpson. Mr. J. W. Lightbown was re-appointed Hon. Recorder and Messrs. D. M. Freeland and J. H. Hamence were re-appointed Hon. Auditors.

The Determination of Poly(Ethyl Esters) in Methyl Methacrylate Copolymers

BY J. HASLAM, J. B. HAMILTON AND A. R. JEFFS

(*Imperial Chemical Industries Ltd., Plastics Division, Welwyn Garden City, Herts.*)

A method has been devised for the determination of poly(ethyl esters), *e.g.*, poly(ethyl acrylate), in methyl methacrylate copolymers. The alkoxyl groups in the sample are converted to the corresponding iodides, which are then determined by gas - liquid chromatographic test.

THE determination of small proportions of poly(ethyl esters) in methyl methacrylate copolymers is an interesting analytical problem. Its solution appeared to depend on a quantitative determination of the total alkoxyl groups present in the polymer, followed by an effective separation of the individual alkyl iodides formed.

Our original efforts were directed to finding a simple process by which, for example, the methoxyl group of poly(methyl methacrylate) could be converted to methyl iodide in very high yield. Such a process has been devised and is essentially based on the method for determining alkoxyl groups in cellulose ethers worked out by Easterbrook and one of us (J. B. H.).[1] The method that we adopted differs from that of Easterbrook and Hamilton only in the following respects—

(*a*) nitrogen was used in conjunction with a mercury lute and a flowmeter as the sweeping-out gas, instead of carbon dioxide,

(*b*) the spiral scrubber contained 4 ml of 25 per cent. w/v sodium acetate solution, and

(*c*) the bromine solution absorber was modified so that a second bromine solution absorber could be fitted in series, as a precautionary measure.

Preliminary experiments showed that the phenol used in Easterbrook and Hamilton's method to solubilise the cellulose ether was also necessary when working with polymers. Experiments carried out without phenol gave only two-thirds of the theoretical yield of alkyl iodide.

When this modified method was applied to known samples (about 20 mg) of disintegrated poly(methyl methacrylate) sheet, samples of poly(methyl methacrylate) moulding granules and a sample of poly(ethyl acrylate), the results shown in Table I were obtained.

From these results it was seen that the recovery of iodides was sufficiently satisfactory for a ratio method to be used for the determination of the relative proportions of the two iodides. It was now necessary to distinguish between the iodides in a quantitative manner.

TABLE I

DETERMINATION OF ALKOXYL CONTENT BY A MODIFIED METHOD

Theoretical methoxyl content of poly(methyl methacrylate) = 31·03 per cent. w/w
Theoretical ethoxyl content of poly(ethyl acrylate) = 45·06 per cent. w/w

Sample	Alkoxyl content, %	Conversion, %
Sample A [disintegrated unplasticised poly-(methyl methacrylate) sheet]	30·45, 30·56 (–OCH₃)	98·2, 98·6
Sample B [disintegrated unplasticised poly-(methyl methacrylate) sheet]	30·23, 30·21 (–OCH₃)	97·5, 97·5
Sample C [poly(methyl methacrylate) mould-ing granules]	30·32, 30·27 (–OCH₃)	97·8, 97·7
Sample D [poly(methyl methacrylate) mould-ing granules]	29·98, 29·94 (–OCH₃)	96·7, 96·6
Sample E [poly(ethyl acrylate)]	44·09, 44·13 (–OCH₂CH₃)	97·8, 97·9

Many methods of separating mixed alkyl iodides derived from alkoxyl groups have been suggested, and a review of these was included in a paper on the subject by Gunnar Gran.[2] However, gas - liquid chromatography seemed to offer great advantages over ordinary chemical methods. Indeed, a paper entitled "Selective Microdetermination of Alkoxy Groups by Gas - Liquid Chromatography" by Martin and Vertalier[3] was read at the Congress on Analytical Chemistry, Lisbon, September, 1956.
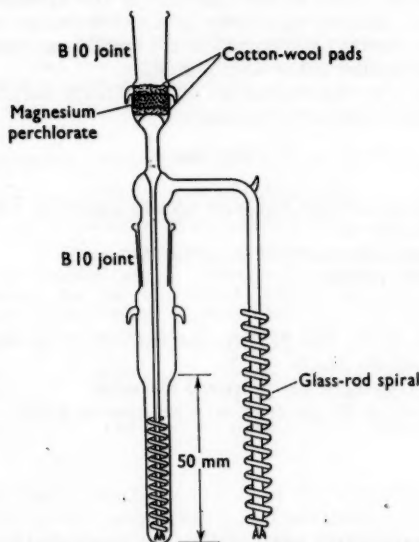
Fig. 1. *n*-Heptane trap with an extension for an absorber containing buffered bromine solution

In their paper these authors were concerned with monomeric substances and distilled the iodides liberated by the Zeisel method into an absorber containing 0·2 ml of chloroform, which in turn contained 5 per cent. w/v of methylene dichloride. The latter acted as an internal standard in their subsequent gas - liquid chromatographic procedure. For methoxyl and ethoxyl groups, Martin and Vertalier found it was possible to ascertain the ratio in which the groups occurred in a single molecule (molar ratio) and to determine them at the same time in an approximate manner (with an error of 5 to 10 per cent.) by working on 20 mg of substance. This knowledge permitted the exact determination of each group when this information was supplemented by an iodimetric determination of the total alkoxyl groups.

Since copolymers may contain the polymerised esters in any ratio, it seemed important to devise an absorber for retaining the liberated iodides quantitatively. The absorber shown in Fig. 1 was found to be satisfactory and was used in all our work. This contained 0·5 ml of solvent and was attached to the spiral scrubber of the apparatus used by Easterbrook and Hamilton. A drying agent was included, since water interfered with the gas - liquid chromatographic procedure. It was necessary that the solvent employed in the absorber should not interfere with the separation of the two iodides in the subsequent chromatographic test and several solvents were tried, the trap being kept at 0° C and at −80° C (*i.e.*, the temperature of a solid carbon dioxide - methanol mixture). Eventually, pure synthetic *n*-heptane was used at −80° C and proved ideal for the purpose. Its efficiency was evaluated by connecting a second absorber containing buffered bromine solution in series with the *n*-heptane absorber to retain any iodides escaping absorption. Determination of the iodides in this buffered bromine solution indicated the proportion of the alkoxyl groups converted to iodide that were retained in solution by the *n*-heptane absorber. The results, which are based on the mean values for alkoxyl content given in Table I, were 99·4 and 99·2 per cent. of methyl iodide retained by the *n*-heptane absorber for Sample A and 99·9 and 99·9 per cent. of ethyl iodide for Sample E.

Further preliminary experiments showed that, if *n*-heptane containing a small amount of methylene dichloride as internal standard was employed as absorbing solvent, loss of methylene dichloride (about 5 to 10 per cent.) resulted with the passage of nitrogen through the absorber even at −80° C. This was overcome by absorbing the alkyl iodides initially in 0·500 ml of *n*-heptane; after absorption was complete 0·500 ml of *n*-heptane, containing internal standard, was then added to the contents of the absorber. In fact, we found it advantageous to use two internal standards in the *n*-heptane—methylene dichloride for comparison with the larger methyl iodide peak and a smaller amount of ethylidene dichloride for comparison with the smaller ethyl iodide peak.

Our full method for the determination of poly(ethyl acrylate) in copolymers with poly(methyl methacrylate) is described below.

METHOD

APPARATUS—

The reaction flask, spiral scrubber and glass spoon as used by Easterbrook and Hamilton, and *the absorber* shown in Fig. 1.
Conventional gas - liquid chromatographic apparatus.
Agla micrometer-syringe pipette.

REAGENTS—

Hydriodic acid, sp.gr. 1·17—The M.A.R. reagent, which is supplied in 6-ml ampoules.
Phenol—Analytical-reagent grade.
n-*Heptane*—The pure synthetically prepared material.
Sodium acetate solution—A 25 per cent. w/v solution in water.
Methylene dichloride.
Ethylidene dichloride.
Methyl iodide.
Ethyl iodide.

PROCEDURE FOR CALIBRATING THE GAS - LIQUID CHROMATOGRAPHIC APPARATUS—

The column used consisted of a U-tube having a total length of 6 feet and a nominal bore of 0·25 inches, packed with a 30 per cent. w/w mixture of dinonyl sebacate on Celite 545 that had been graded as described by Martin and James.[4]

The conditions were as follows—

Column temperature,	75° C;
Inlet pressure,	550 mm of mercury;
Exit pressure,	150 mm of mercury;
Nitrogen flow-rate,	3·0 litres per hour;
Bridge current,	140 mA;
Katharometer temperature,	room temperature (22° C).

Add 0·500 ml of methylene dichloride and 0·250 ml of ethylidene dichloride accurately to *n*-heptane contained in a 100-ml calibrated flask by means of an Agla micrometer-syringe pipette. Dilute the contents of the flask to the mark with *n*-heptane and shake thoroughly.

1 ml of this n-heptane solution contains 0·005 ml of methylene dichloride and 0·0025 ml of ethylidene dichloride.

To 10·0-ml aliquots of the n-heptane solution add various known volumes of methyl and ethyl iodides accurately by micrometer-syringe pipette (see Table II).   Subject 2 to 5 drops of each of these solutions to gas - liquid chromatographic test under the above-mentioned conditions (the actual amount depending on the iodide content).   From the chromatograms determine the ratios of (a) peak height of methyl iodide to the peak height of 0·005 ml of methylene dichloride and (b) peak height of ethyl iodide to peak height of 0·0025 ml of ethylidene dichloride, and construct calibration curves, with the weights of iodide as ordinates and these ratios as abscissae.   Our results are summarised in Table II and the calibration curves are shown in Fig. 2.
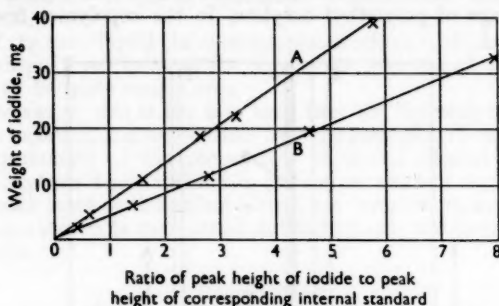

Fig. 2.   Calibration curves: curve A, methyl iodide; curve B, ethyl iodide

TABLE II

RESULTS OBTAINED IN THE CONSTRUCTION OF THE CALIBRATION CURVES

$d^{20°C}_{4°C}$ for methyl iodide 2·279

$d^{20°C}_{4°C}$ for ethyl iodide 1·933

Standard No.	Volume of methyl iodide added, ml	Weight of methyl iodide, mg per ml of solution	Volume of ethyl iodide added, ml	Weight of ethyl iodide, mg per ml of solution	Ratio (a)	Ratio (b)
1	0·170	38·63	—	—	5·79	—
3	—	—	0·170	32·86	—	7·95
3	0·100	22·79	0·010	1·93	3·33	0·42
4	0·080	18·23	0·030	5·79	2·62	1·40
5	0·050	11·40	0·060	11·58	1·66	2·87
6	0·020	4·56	0·100	19·33	0·67	4·68

PROCEDURE—

Clean the reaction flask, spiral scrubber and the n-heptane absorber assembly with chromic - sulphuric acid mixture and wash them thoroughly with distilled water.   Dry the apparatus by washing it with acetone and allowing residual acetone to evaporate.   Place 2·5 g of phenol and the contents of a 6-ml ampoule of hydriodic acid in the reaction flask.   Put 4 ml of 25 per cent. w/v sodium acetate solution in the spiral scrubber and place the stopper in the open end.   Connect the spiral scrubber to the reaction flask with suitable tension springs.   With water flowing through the condenser and a nitrogen flow of 6 ml per minute passing through the apparatus, heat the contents of the reaction flask to boiling and maintain gently boiling for 30 minutes.   This serves to condition the apparatus for the test.   Withdraw the burner and allow the reaction flask to cool.   Measure accurately 0·500 ml of n-heptane into the absorber by micrometer-syringe pipette and fit the absorber assembly to the spiral scrubber by means of tension springs.   Weigh out accurately about 20 mg of copolymer into the glass spoon and lower the spoon plus sample carefully down through the condenser into the reaction flask.   Reconnect the spiral scrubber and when assembled submerge the n-heptane absorber in solid carbon dioxide - methanol mixture.

Heat the contents of the reaction flask to boiling and maintain boiling for 1 hour. Disconnect the absorber assembly. Add 0·500 ml of a *n*-heptane solution containing 1 per cent. v/v of methylene dichloride and 0·5 per cent. v/v of ethylidene dichloride (made up accurately by micrometer-syringe pipette) to the contents of the absorber by micrometer-syringe pipette and mix the solutions. Hence the absorber now contains 0·005 ml of methylene dichloride, 0·0025 ml of ethylidene dichloride, *n*-heptane up to 1 ml and the evolved iodides. Subject 1 to 6 drops of this heptane solution to chromatographic test under the conditions of calibration.

With copolymers having a low poly(ethyl acrylate) content, it is necessary to run two chromatograms to find the ratios (*a*) and (*b*), *i.e.*, 1 drop of solution to obtain ratio (*a*) and 5 or 6 drops of solution to find ratio (*b*) (see Fig. 3). This would be unnecessary with a gas - liquid chromatograph fitted with an attenuator. Calculate the ratios (*a*) and (*b*) and from the calibration curves find the weights of each iodide evolved from the polymer. Calculate the percentage of poly(ethyl acrylate) in the copolymer from the yield of the two iodides.
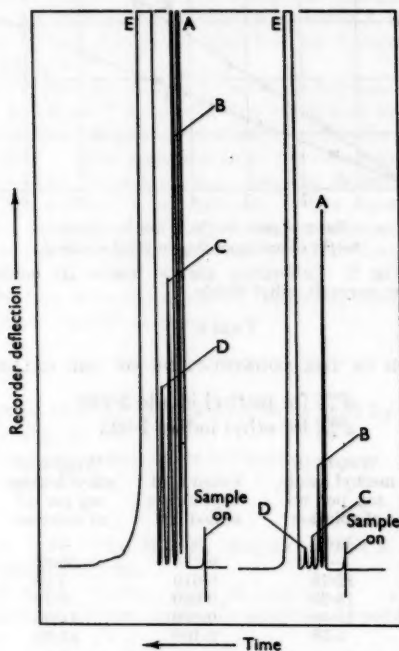
Fig. 3. Chromatograms: (*a*), 6 or 7 drops of trap solution; and (*b*), 1 drop of trap solution. A, methyl iodide; B, methylene dichloride; C, ethylidene dichloride; D, ethyl iodide; E, *n*-heptane

RESULTS

A 19·9-mg sample of a copolymer known to consist of 91 per cent. of poly(methyl methacrylate) and 9 per cent. of poly(ethyl acrylate) was subjected to the procedure described above. The chromatograms obtained are shown in Fig. 3. The peak heights of methyl iodide, methylene dichloride, ethylidene dichloride and ethyl iodide were measured and the ratios (*a*) and (*b*) were calculated. These ratios were 3·75 and 0·66, respectively. By means of the calibration curve it was found that the trap therefore contained—

25·6 mg of methyl iodide ≡ 18·05 mg of poly(methyl methacrylate) and
2·8 mg of ethyl iodide ≡ 1·80 mg of poly(ethyl acrylate).

(NOTE—Methyl methacrylate and ethyl acrylate are isomeric and have a molecular weight of 100·11.)

$$\therefore \text{ Recovery (in terms of original polymer)} = 19\cdot85 \text{ mg.}$$

$$\therefore \text{ Poly(ethyl acrylate) in copolymer} = \frac{1\cdot80}{19\cdot85} \times 100$$

$$= 9\cdot07 \text{ per cent.}$$

Other results found for this copolymer were 9·04 and 9·09 per cent.

Similarly for a copolymer known to consist of 97 per cent. of poly(methyl methacrylate) and 3 per cent. of poly(ethyl acrylate), the results were 2·96, 3·15 and 3·09 per cent. When our control samples, *i.e.*, Samples A and E in Table I, were subjected to the complete procedure as described above, Sample A [poly(methyl methacrylate)] yielded no trace of ethyl iodide and Sample E [poly(ethyl acrylate)] yielded no trace of methyl iodide. Incidentally, experiments in the presence of dibutyl phthalate indicate that this plasticiser does not interfere with the test.

The accuracy of the gas - liquid chromatographic method, with close control, is generally accepted as being within 2 per cent. of the percentage determined and within these limits we believe our test to be quite satisfactory.

As far as we are aware, this is the first time that the determination of alkoxyl groups in polymers has been recorded, and we consider that the principles of our test may prove useful in the general determination of the proportions of mixed alkoxyl groups in monomeric substances. The *n*-heptane trap, which has proved so efficient for absorbing methyl and ethyl iodides, may (with some modification) have other useful applications, *e.g.*, for absorbing substances from the gas stream in gas - liquid chromatography for examination by ultra-violet and infra-red methods.

REFERENCES

1. Easterbrook, W. C., and Hamilton, J. B., *Analyst*, 1953, **78**, 551.
2. Gran, G., *Svensk Papperstidning*, 1954, **57**, 702.
3. Martin, F., and Vertalier, S., Presented at the XVth International Congress on Pure and Applied Chemistry (Analytical Chemistry), Lisbon, September 8th to 16th, 1956.
4. Martin, A. J. P., and James, A. T., *Biochem. J.*, 1952, **50**, 679.

The Separation of Quaternary Halides by Paper Chromatography

BY H. HOLNESS* AND W. R. STONE

(*Chemistry Department, South West Essex Technical College, Walthamstow, London, E.17*)

Separations within the homologous series of certain surface-active cationic germicides by means of paper chromatography are described. By using a new spray reagent, the detection on the paper of as little as 0·6 μg of the quaternary base is possible.

WITHIN recent years increasing use has been made in both industry and medicine of germicides whose activity is derived from the presence of surface-active quaternary ammonium or pyridinium salts, and this entails a need for their recognition. Since the publication of our Note[1] on the paper chromatography of cationic surface-active agents, three papers[2,3,4] have been published on this subject.

An electrochromatographic method used by Fumasoni, Mariani and Torraca[2] for the separation of the homologous series of *n*-alkylpyridinium halides requires amounts of material greater than 50 μg and the spots formed exhibit "tailing." An ascending chromatogram described by Garcia and Couerbe[3] separates commercial products having mixtures of chain lengths in the *n*-alkyl radical, but the minimum amount detectable is 5 μg. Negoro and Seno[4] also used electrochromatography to separate quaternary bases from non-ionic surface-active agents when present in admixture, but they again experienced considerable "tailing."

The method described in this paper allows separations within the homologous series of saturated *n*-alkyltrimethylammonium halides, *n*-alkylbenzyldimethylammonium halides and

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n-alkylpyridinium halides when the alkyl chain possesses from twelve to eighteen carbon atoms. The limit of detection is of the order of 0·6 μg.

EXPERIMENTAL

APPARATUS AND TECHNIQUE—

All the chromatograms were prepared by using the ascending-solvent technique and Whatman No. 1 paper (for chromatography). Two types of container were used, the first a rectangular tank, which allowed two sheets, 15·75 cm × 33·5 cm, to be run simultaneously. The second container was a large cylinder with vertical sides 30 cm high and with a diameter of 15 cm. This allowed one sheet, 33·5 cm × 31·5 cm, to be used, this sheet being rolled into a tube as described by Wolfson, Cohn and Devaney.[5] In this manner a dozen spots could be run on the one sheet. The containers were closed and sealed by covering the top with a sheet of polythene film and securing it round the sides with a strong rubber band. Both the containers were placed in a thermostatically controlled oven adjusted to a temperature of 30° C.

All the quaternary salts used in this work were white crystalline products and were supplied as single substances containing only the n-alkyl chain length indicated by its name. For application to the chromatogram, the salts were dissolved in 50 per cent. aqueous ethanol to concentrations that allowed volumes not greater than 0·003 ml to be spotted on the paper. These spots were applied along a line 3 cm from the base by means of a capillary pipette graduated in 0·001 ml. When the chromatograms had run the required distance, they were removed from the container and allowed to dry by exposure to air at room temperature. In this connection it is of interest to note that at a certain time in the process of drying, the separated spots of the quaternary base became faintly visible by reflected light as lighter and more opaque areas on the still damp paper. It is thought that this might be due to a decreased rate of evaporation of the solvent from the paper in the presence of the surface-active agent. It is, however, unlikely that this could be of general use for determining the position of the spots, since the phenomenon was only observed when the material was present in relatively high concentrations.

When the papers were dry, they were sprayed with the reagent and examined under ultra-violet light while damp. The spots of the quaternary base fluoresced a bright vermilion on a bright white background only faintly tinged with pink; their positions were marked by means of a soft pencil.

REAGENTS—

The solvent mixtures used in developing the chromatograms, 35 per cent. and 40 per cent. aqueous ethanol, were prepared by mixing 35 and 40 ml, respectively, of 96 per cent. v/v industrial methylated spirit with 5 ml of concentrated hydrochloric acid and diluting each mixture to 100 ml with water.

The indicator spray reagent was freshly prepared immediately before use by mixing 5 ml of a 0·2 per cent. w/v aqueous solution of rhodamine BS with 10 ml of a 0·2 per cent. w/v aqueous solution of Tinopal WG, adding 40 ml of ammonia solution, sp.gr. 0·880, and diluting with water to 100 ml.

RESULTS

With both the developing solvents clear separations were obtained within each homologous series of the lauryl, myristyl, cetyl and stearyl derivatives. The R_F values quoted in Table I represent the average in each case of at least thirty determinations carried out with a solution containing equal weights of each member in the series. It was unfortunate that no pure sample of benzyldimethylmyristylammonium chloride was available and the R_F value quoted in this instance is that found when a commercial product was examined.

It will be seen that the benzyldimethyl-laurylammonium, benzyldimethylmyristylammonium and benzylcetyldimethylammonium halides can be differentiated from the corresponding n-alkyltrimethylammonium and n-alkylpyridinium halides, but only poor separation of the stearyl derivatives is shown. The R_F values of the n-alkyltrimethylammonium and n-alkylpyridinium salts in both solvents are practically identical and separations could not be achieved, although the pyridinium salts generally showed slightly lower R_F values. Better separations might well be achieved by allowing the solvent to run a greater distance, but limitation of the size of the containers available did not allow the examination of this possibility.

TABLE I

R_F VALUES FOR PURE COMPOUNDS

Paper, Whatman No. 1   Time of run, 7 hours approximately
Temperature, 30° C   Length of run, 27 cm approximately

n-*Alkyltrimethylammonium salts*—			R_F with 35 per cent. ethanol	Standard deviation	R_F with 40 per cent. ethanol	Standard deviation
Lauryl	..	..	..	0·86	0·03	0·92	0·02
Myristyl	..	..	..	0·65	0·03	0·79	0·02
Cetyl	..	..	..	0·36	0·02	0·55	0·04
Stearyl	..	..	..	0·10	0·01	0·23	0·04
n-*Alkylbenzyldimethyl-ammonium salts*—						
Lauryl	..	..	..	0·71	0·04	0·85	0·02
Myristyl*	..	..	..	0·39	0·02	0·61	0·01
Cetyl	..	..	..	0·20	0·04	0·40	0·03
Stearyl	..	..	..	0·06	0·01	0·14	0·03
n-*Alkylpyridinium salts*—						
Lauryl	..	..	..	0·81	0·03	0·90	0·01
Myristyl	..	..	..	0·58	0·05	0·75	0·02
Cetyl	..	..	..	0·31	0·04	0·54	0·03
Stearyl	..	..	..	0·08	0·02	0·20	0·03

* These values were found by using a commercial material of mixed chain lengths.

In Table I the figures for the standard deviations are derived from the values for several separate runs. Some of these values are rather large, but this is due to variation from one sheet of paper to another. When several spots of identical material are run simultaneously on the same sheet of paper, the spread of R_F values for each component is seldom greater than $\pm 0·01$. It is therefore recommended that, for purposes of identification, control spots of known composition should be run on the same sheet as spots of an unknown mixture.
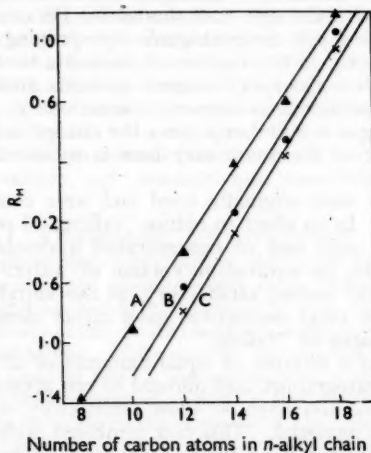
Fig. 1. Graph of R_M values plotted against *n*-alkyl chain length, with the 35 per cent. ethanol mixture as developing solvent: curve A, *n*-alkylbenzyldimethylammonium homologues; curve B, *n*-alkylpyridinium homologues; curve C, *n*-alkyltrimethylammonium homologues

The R_M value, log $(1/R_F - 1)$, proposed by Bate-Smith and Westall,[6] was evaluated from the R_F values shown in Table I and the values obtained within each homologous series were plotted against the corresponding number of carbon atoms in the *n*-alkyl chain. The points

on each graph fell close to the straight line drawn through points calculated by the method of least squares to give the best fit to the experimental data. It is of interest to note that the R_M value obtained from the graph for the *n*-octyl, *n*-decyl and *n*-tetradecyl derivatives of the homologous series of *n*-alkylbenzyldimethylammonium salts were in close agreement with those found experimentally from the chromatogram of the commercial alkylbenzyldimethylammonium halide by using the 35 per cent. ethanol solvent. With 40 per cent. ethanol as solvent (see Fig. 1), the *n*-octyl and *n*-decyl derivatives formed only one spot near the solvent front.

LIMIT OF DETECTION—

The lower members of the series gave definite spots when present to the extent of 0·2 μg, but the cetyl and stearyl derivatives required 0·6 μg for positive identification.

DISCUSSION

In the initial stages of the work the chromatograms were run at room temperature, but it soon became evident that the variation in temperature was having an effect on the R_F values. It was therefore decided to run the chromatograms at a temperature sufficiently above average room temperature to allow thermostatic control. The temperature selected was 30° C and was obtained by using an electric oven thermostatically controlled to $\pm 1°$ C.

In a search for a sensitive means of revealing the position of the spots of the quaternary base on the developed chromatogram, a similar line of reasoning was followed to that which led to the formulation of the mixed indicator used in the scheme of semi-micro qualitative analysis of surface-active agents recently published.[7] Initially, a series of anionic dye-stuffs that had the property of fluorescing in ultra-violet light was tested, and with many compounds it was found that the presence of a quaternary base quenched or modified the colour of the fluorescence. Anionic optical bleaches were also found to have their fluorescence quenched by quaternary bases, but the background was then too bright to give a sensitive contrast. In order to increase this contrast, fluorescent cationic dyestuffs were added to the optical bleach and this improved the sensitivity. The most sensitive reagent found was the optical bleach Tinopal WG mixed with the dye-stuff rhodamine BS or rhodamine B500.

Previously,[1] we developed the chromatogram by spraying with a solution of these two materials and then exposing to the vapours of ammonia to neutralise any mineral acid remaining on the paper. Here the spray reagent contains ammonia in solution and the additional stage of exposing to ammonia vapours is unnecessary. The position of the spots must be marked while the paper is still damp, since the change in fluorescence in ultra-violet light caused by the presence of the quaternary base is substantially eliminated when the paper is dry.

Several solvent systems were originally tried and were composed of various concentrations of aqueous ethanol. In an effort to reduce "tailing," 5 per cent. v/v of ammonium hydroxide, of glacial acetic acid and of concentrated hydrochloric acid were added in turn to the solvent, replacing an equivalent volume of water. Of these additions only concentrated hydrochloric acid proved satisfactory, as the lauryl and myristyl derivatives gave good circular spots, the cetyl derivatives gave rather elongated ovals and only the stearyl derivatives showed signs of "tailing."

It was found that, when a mixture of equal amounts of all four members of a given homologous series was chromatographed and allowed to run approximately 27 cm, the spots of the lower members became too large to allow satisfactory separation when each spot contained more than 6 μg of material. This fact combined with the limit of detection of the spray reagent would suggest that approximately 10 per cent. of any particular chain length within a mixture of members of an homologous series could be detected when run from a single spot under the experimental conditions described. It would seem possible that a smaller percentage of any given chain length in a mixture of chain lengths might be detected if the solvent were allowed a longer run. This would allow a greater separation between adjacent spots with the consequence that each could contain more than 6 μg of material.

Geigy & Co. Ltd. for the Tinopal WG and Imperial Chemical Industries for the rhodamine dye-stuff.

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Precise Determination of Plutonium by Differential Spectrophotometry

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A method is described for the determination of milligram amounts of plutonium by differential spectrophotometry with a precision (σ) of ± 0.05 per cent. The sample is dissolved in hydrochloric acid and maintained in the reduced state by the presence of hydroxylamine hydrochloride in the solution. The relative absorbancy of the sample is then measured against that of an accurately known standard solution at 5650 A. The optimum solution conditions to give highest precision have been selected and the effect of the presence of some foreign cations has been investigated.

THE metallurgical investigation of plutonium alloys necessitates the development of accurate methods of analysis for that element. A gravimetric[1] and volumetric methods[2,3] are available, but are subject to interference from other elements. Spectrophotometry offers the possibility of determining the plutonium content of an alloy with the minimum of chemical pre-treatment, a factor of some importance when dealing with radio-toxic materials. To achieve absorptiometrically the accuracy normally required for major constituents of an alloy, a differential technique[4,5,6] must be employed. Differential absorptiometry with use of a Spekker absorptiometer has been employed in the analysis of plutonium alloys by Atkins and Jenkins,[7] but it was considered that the use of a spectrophotometer offered the advantage of improved precision, *e.g.*, uranium has been determined with a precision of 1 part in 1000.[8,9]

PRELIMINARY CONSIDERATIONS

Aqueous solutions of plutonium may contain the metal in the ter-, quadri- and sexa-valent forms, or less commonly the quinquivalent form, the spectra of which all show the characteristic narrow absorption bands.[10] Chemically it is convenient to work with the lowest valency that is relatively stable in acid solution in the presence of excess of reductant, *e.g.*, hydroxylamine hydrochloride. Plutonium[III] has narrow peaks at 5650 A ($\epsilon = 35.5$) and 6030 A ($\epsilon = 35.0$); the peak at 5650 A was selected for a number of reasons. Although previous investigators have usually worked at 6030 A, they have done so to permit the determination of plutonium[III] to be made in the presence of plutonium[IV] and plutonium[VI]. For the determination of total plutonium, it is not necessary to employ a wavelength that is characteristic of one valency state, and hence it is better to work at 5650 A. From the instrumental point of view, the transmission of the optical system of the Beckman spectrophotometer is at a maximum at about 5000 A, and so narrower slit widths can be used, and this results in a greater intrinsic scale length. Finally, the peak at 5650 A has a lower temperature coefficient[10] and is less subject to changes of anion concentration.[11] It will be shown that Beer's law is obeyed up to absorbancies of 2.0, when the slit width is 0.34 mm.

EXPERIMENTAL

A series of standard plutonium solutions having concentrations of from 5 to 40 mg per ml was prepared by dissolving weighed amounts of the pure metal in dilute hydrochloric

acid. Impurity analyses on the metal in other laboratories had revealed less than 0·1 per cent. total weight of all likely impurities. The metal was freshly cut in an atmosphere of argon and was weighed before appreciable surface tarnishing had occurred. The solutions were finally diluted to a known volume in molar hydrochloric acid and 5 per cent. w/v hydroxylamine hydrochloride at 25° C. This procedure is known to give plutonium[III]. By using aliquots from the standard solutions and diluting them to 25·0 ml with a molar solution of hydrochloric acid containing 5 per cent. w/v hydroxylamine hydrochloride, a series of calibration curves was prepared with use of reference standards of increasing concentration and by adjusting the slit width as necessary to achieve balance (see Fig. 1). These calibration curves show marked deviations from linearity at the higher concentrations. By using methods described by Hiskey and Young, the optimum concentration of the reference solution to give greatest precision was calculated. The calculations indicate that the optimum concentration is in the region of 8 mg per ml and it is seen that, at slit widths greater than 0·35 mm, the beam band width is greater than the absorption band width at 5650 A with consequent loss of precision. An accurate calibration graph was next prepared with use of a reference standard having a concentration of 8·23 mg per ml and a series of solutions of various concentrations up to 13·90 mg per ml. All these solutions were made to volume in molar hydrochloric acid and 5 per cent. w/v hydroxylamine hydrochloride at 25° ± 0·2° C.
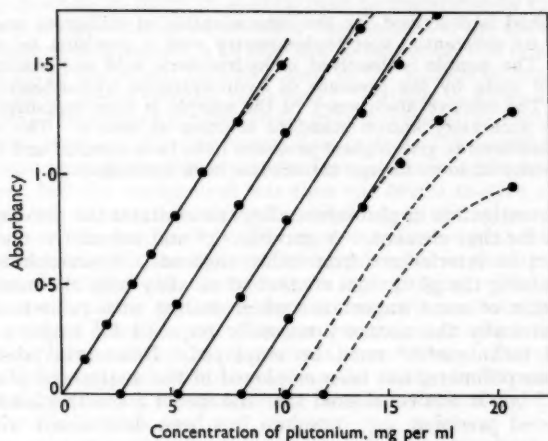
Fig. 1. Absorbancy results for solutions of plutonium[III]

The cell compartment of the spectrophotometer was also maintained at this temperature during absorption measurements. The results were as follows—

Concentration of plutonium, mg per ml	8·23	9·49	10·27	11·12	12·84	13·90
Relative absorbancy (1-cm cells and slit width of 0·34 mm) ..	0·000	0·180	0·296	0·421	0·659	0·820
Absolute absorbancy	1·240	1·420	1·536	1·661	1·899	2·060

From the results it is seen that when a reference standard containing 8·23 mg of plutonium per ml is used the concentration of an unknown sample in the range 8·23 to 13·90 mg per ml can be determined with a precision (σ) of ±0·05 per cent. It was convenient for working purposes to calculate a calibration factor from the values given above. The calculation was as follows—

Δ Concentration of plutonium, mg per ml ..	1·26	2·04	2·89	4·61	5·67	Total = 16·47
Δ Absorbancy	0·180	0·296	0·421	0·659	0·820	Total = 2·376

$$\text{Calibration factor} = \frac{16\cdot47}{2\cdot376} = 6\cdot93 \text{ mg per ml per unit of absorbancy.}$$

EFFECT OF VARIATION OF CONDITIONS—

The solution conditions used were selected more or less arbitrarily and it was necessary to decide how critical slight variations might be.

Temperature—From previous work[7] it was known that the slope of the calibration curve would decrease with temperature. This was confirmed and the rate of change was determined by measuring the difference in absorbancy between two standard solutions, each at the same temperature, over the range 16° to 35° C, the results being as follows—

Temperature, °C		16	21	25	30	35
Relative absorbancy		+0·304	+0·294	+0·287	+0·279	+0·273

The absolute absorbancy was 1·5 and the results gave a slope of $-0·0016$ units of absorbancy per °C. In terms of absolute absorbancy this is equivalent to an error of 0·1 per cent. per °C. It is therefore necessary, for highest accuracy, to measure absorbancy differences within $\pm 0·5°$ C of the temperature used for preparation of the calibration curve.

Hydrochloric acid concentration—A series of solutions of identical plutonium concentration, but containing different concentrations of hydrochloric acid, was prepared. By using the solution that was molar in hydrochloric acid as the reference standard, the other solutions were compared differentially with it. No systematic trend was observed, the variations in relative absorbancy being of a random nature. The results were as follows—

Concentration of hydrochloric acid, M		1·0	0·55	0·75	1·25	1·50	2·0
Relative absorbancy		0·000	+0·002	−0·004	0·000	+0·001	−0·003

The absolute absorbancy was 0·765 and the precision (σ) of the results was $\pm 0·2$ per cent.

Hydroxylamine hydrochloride concentration—The effect of variation of the concentration of hydroxylamine hydrochloride was tested by the same differential technique as described above. Again only random variations in absorbancy difference were observed, the results being as follows—

Concentration of hydroxylamine hydrochloride, % w/v	5	1	2·5	5·0	7·5	10·0
Relative absorbancy	0·000	−0·002	−0·002	−0·001	−0·001	+0·002

The absolute absorbancy was 0·765 and the precision (σ) of the results was $\pm 0·2$ per cent.

Nitric acid concentration—In the separation of plutonium from uranium as described by Atkins and Jenkins,[7] there is the possibility of some nitric acid being present in the plutonium fraction. The effect of added nitric acid on the relative absorbancy of a number of solutions was tested. It was found that moderate concentrations of nitric acid, *e.g.*, 3 M, had no effect on the relative absorbancy measured. The results were as follows—

Concentration of nitric acid, M	0·0002	0·001	0·002	0·004	0·01	0·04	0·08	0·2	0·6	1·3	3·2
Relative absorbancy	0·000	0·000	−0·005	+0·005	−0·004	0·000	−0·002	−0·001	+0·006	+0·010	0·000

The absolute absorbancy was 0·765 and the precision (σ) of the results was $\pm 0·33$ per cent.

It should be noted that, in the tests to determine the effect of variation of concentrations of hydrochloric acid, hydroxylamine hydrochloride and nitric acid, the concentration of plutonium in the solutions used was unavoidably lower than is required for highest precision.

INTERFERENCE BY ADDED CATIONS—

The effect of adding cations likely to be met in the analysis of plutonium alloys was tested in the same manner as was used for the solution conditions. Reference standards and proposed solutions of identical plutonium concentrations were used, the absolute absorbancy being 1·5, and various amounts of the second cation were added to the prepared solutions. The standard and sample solutions were then adjusted to volume and compared differentially. The results are given in Table I. From this it is seen that excess of thorium, uranium, calcium and cerium (cerous) can be present in the solution without greatly affecting the precision of the plutonium determination. Iron added as ferric chloride interferes seriously, even at ratios of iron to plutonium as low as 0·1. Greater amounts can be tolerated, up to a ratio of 1·0, by the inclusion of 5 ml of a 5 per cent. w/v solution of stannous chloride in the 25 ml of alloy solution. Aluminium causes a slight decrease in absorbancy at ratios of 1·5 and greater. Zirconium increases the absorbancy of a plutonium solution. This was observed to be due to a slight turbidity formed on the addition of zirconium (as the oxychloride) to the solution.

ANALYSIS OF PLUTONIUM - THORIUM ALLOYS

It has been shown that excess of thorium does not interfere in the differential spectrophotometric determination of plutonium. Accordingly, the plutonium contents of some plutonium - thorium binary alloys were determined, without separation, by direct comparison

of the absorbancy of the alloy solution in molar hydrochloric acid and 5 per cent. w/v hydroxylamine hydrochloride against that of a plutonium standard of concentration 8·30 mg per ml. The results are shown in Table II.

TABLE I

EFFECT OF ADDED CATIONS

Added cation	Ratio of added cation to plutonium	Relative absorbancy	Precision (σ) when no definite trend is observable, %	Added cation	Ratio of added cation to plutonium	Relative absorbancy	Precision (σ) when no definite trend is observable, %
Thorium	0·80	−0·001		Uranium	0·4	−0·002	
	1·55	−0·004	} ±0·15		1·0	+0·005	
	3·90	+0·003			2·0	+0·004	
					4·0	−0·003	} ±0·31
Iron (as Fe³⁺)	0·13	+0·012			8·0	+0·004	
	0·63	+0·020					
	2·5	+0·085		Zirconium	1·0	+0·020	
	6·3	+0·213			5·0	+0·050	
					6·0	+0·065	
Iron (in presence of stannous chloride)	1·6	+0·007					
	3·2	+0·028		Calcium	1·2	−0·004	
	4·9	+0·026			2·4	−0·001	} ±0·17
	6·5	+0·122			6·0	+0·002	
Aluminium	1·5	−0·020		Cerium	1·7	+0·002	
	3·8	−0·038			3·4	−0·001	} 0·08
	5·3	−0·050			8·5	0·000	

TABLE II

ANALYSIS OF PLUTONIUM - THORIUM ALLOYS

Alloy No.	Relative absorbancy of solution	Relative concentration of plutonium, mg per ml	Absolute concentration of plutonium, mg per ml	Plutonium in alloy, %	Thorium in alloy, %	Total, %
1	+0·017	+0·12	8·42	96·0 ± 0·1	3·9 ± 0·2	99·9
2	+0·050	+0·35	8·65	94·8 ± 0·1	4·8 ± 0·2	99·6
3	+0·300	+2·08	10·38	94·2 ± 0·1	5·8 ± 0·2	100·0
4	+0·639	+4·42	12·72	67·3 ± 0·07	32·8 ± 0·1	100·1
5	+0·034	+0·24	8·54	42·8 ± 0·04	57·4 ± 0·1	100·2

METHOD

REAGENTS—

Hydrochloric acid, sp.gr. 1·18—Analytical-reagent grade.
Hydroxylamine hydrochloride—Analytical-reagent grade.
Hydroxylamine hydrochloride solution, 5 per cent. w/v—Dissolve 50 g of the hydroxylamine hydrochloride in distilled water and add 90 ml of the hydrochloric acid. Dilute with distilled water to 1 litre.

APPARATUS—

Beckman DU spectrophotometer—For highest precision, the temperature of the water circulated through the cell chamber block must be thermostatically controlled. A more even temperature throughout the cell chamber is attained if excess heat from the lamp housing is prevented from reaching it. This can be done by circulating cooling water through a metal coil welded underneath the lamp housing.

Thermostatically controlled water tank maintained at 25° ± 0·20° C—It is convenient to circulate water from this tank through the cell chamber block.

Beckman 1-cm cells—These must be identifiable and always used in the same position and in the same orientation in the cell carrier. One cell and position is reserved for the reference solution and corrections are applied for any differences in absorbancy due to the sample cells. The correction for each sample cell is determined experimentally by filling both standard and sample cell with the reference solution and comparing the two differentially.

SAFETY PRECAUTIONS—

The general type of facilities necessary for the safe handling of plutonium in laboratories have been described elsewhere.[12] In this work, plutonium samples were dissolved and the temperature of the solutions was thermostatically controlled in a "glove box." The spectrophotometer itself was partly enclosed in a "glove box," in such a way that solutions could be transferred to the cell compartment without exposing them to the open laboratory.

PROCEDURE FOR DETERMINING THE CALIBRATION FACTOR—

Weigh a number of plutonium samples that on dissolution will provide a series of standard solutions of various concentrations within the range 8 to 14 mg per ml. Place each sample in a beaker together with sufficient distilled water completely to immerse the metal. Add hydrochloric acid drop by drop as the reaction proceeds, but do not allow the reaction to proceed too vigorously. On nearing completion, add sufficient hydrochloric acid to make the solution molar in acid. Warm the solution for a few minutes, cool it and then transfer it to a calibrated flask and add sufficient solid hydroxylamine hydrochloride to make the solution 5 per cent. w/v. Thermostatically control the temperature of the solution for 1 hour and then adjust it to volume with hydroxylamine hydrochloride solution. By using the most dilute solution as the reference standard and balancing the instrument at a slit width of 0·34 mm, measure the relative absorbancy of each solution. Make any necessary cell corrections and calculate the calibration factor as shown on p. 76.

PROCEDURE FOR DETERMINING PLUTONIUM—

Dissolve the sample containing plutonium as before. Carry out a preliminary assessment of the concentration of plutonium by direct spectrophotometry. To do this, prepare a dilution of the solution to give an absorbancy of less than 1·0. Knowing the approximate concentration of plutonium in the sample, select a standard the concentration of which is nearest to that of the unknown. Measure the difference in absorbancy between the unknown and the reference standard and calculate the concentration of plutonium by using the calibration factor. Should the reference standard selected be more concentrated than the sample solution, balance the instrument on the more dilute of the two solutions and measure the relative absorbancy, which will be negative.

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The Absorptiometric Determination of Traces of Iron in Bismuth

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The development of an accurate method for the determination of traces of iron in bismuth is described. Of the many reagents considered, 4:7-diphenyl-1:10-phenanthroline was found to be the most suitable, both in specificity and sensitivity.

In a hydrochloric acid solution of the sample, iron^{III} is reduced to iron^{II} by stannous chloride. The 4:7-diphenyl-1:10-phenanthroline is then added, followed by a mixture of disodium ethylenediaminetetra-acetate and sodium citrate. This serves the dual purpose of adjusting the pH and complexing the bismuth, hence preventing its precipitation.

The iron complex is extracted with *n*-hexyl alcohol and the optical density of the solution is measured at 533 mμ.

AN analytical method was required that would permit the iron content of bismuth to be determined accurately in the range 2 to 100 p.p.m., the range 2 to 10 p.p.m. being particularly important. Of the many reagents available,[1] potassium thiocyanate appeared to be an obvious choice and was found to be satisfactory at levels above about 10 μg, but, below this, interference from bismuth and the instability of the coloured complex caused us to abandon its use.

Smith, McCurdy and Diehl[2] describe a new reagent, 4:7-diphenyl-1:10-phenanthroline (bathophenanthroline) for the determination of very small amounts of iron. This reagent is almost specific for iron^{II} and is twice as sensitive as 1:10-phenanthroline, and the ferrous complex can easily be extracted with *iso*amyl alcohol or *n*-hexyl alcohol.

The general behaviour of bathophenanthroline is similar to that of other phenanthrolines, and, since the method of Smith, McCurdy and Diehl, as described, was inapplicable in the presence of bismuth, attention was directed to existing methods applicable to bismuth that make use of 1:10-phenanthroline.[3,4] In general, they appear to suffer from poor reproducibility, together with other undesirable features, such as slow formation of colour, fairly critical adjustment of pH and occasional precipitation of basic bismuth salts. There are also considerable differences of opinion on the choice of reductant for iron^{III} and on the order of addition of the reagents. Since the substitution of bathophenanthroline for 1:10-phenanthroline could not be expected to overcome these difficulties, our attention was turned to the factors affecting the formation of the ferrous phenanthrolines.

At pH 4, in non-complexing media, the rate of formation of ferroin (ferrous 1:10-phenanthroline) from iron^{II} and the usually employed 100 to 200-fold excess of reagent is immeasurably fast. A slow rate of colour formation indicates, therefore, a deficiency of some or all of the reacting ionic species. In the presence of bismuth, the iron complex must be finally formed in the presence of appreciable amounts of reagents such as ethylenediaminetetra-acetic acid (EDTA), tartrate or citrate, the last named being the most effective complexing agent. Both iron^{III} and iron^{II} are complexed by citrate[5] and the greater stability of the iron^{III} complexes makes the reduction of iron^{III} more difficult. Further, there will be competition for iron^{II} between the citrate and the phenanthroline. Hence it may be assumed that attempts to form the ferrous complex in the presence of citrate at pH 4, with reducing agents such as hydroxylamine or hydroquinone, are not likely to be entirely satisfactory.

EXPERIMENTAL

From the above-mentioned consideration, the reduction stage was carried out in 2 *M* acid with tin^{II} as the reductant.

The order of addition of the other reagents was then investigated. It was immediately apparent that the bathophenanthroline must be added before the citrate, otherwise little or no colour was produced and the rate of formation of the colour was far too slow. It was further observed that, when iron^{II} was added to a solution already containing bathophenanthroline and citrate at pH 4, no trace of the coloured complex was visible, even after a long period of time.

From the work of Lee, Kolthoff and Leussing,[6,7] and our observations on the lack of reactivity of iron[II] in the presence of citrate, it appeared likely that the intermediate ionic species occurring in the presumably stepwise formation of $Fe(bathophenanthroline)^{2+}$ are present in relatively concentrated acid solutions. When the pH is subsequently raised to 4, the final complex should be formed rapidly and quantitatively. The rate of formation of the ferrous complex was, however, still slow, and this could only be attributed to too small a concentration of bathophenanthroline. Owing to the low solubility of bathophenanthroline in water, further addition of the reagent was impracticable, but the addition of 10 ml of ethanol before the addition of the citrate ensured that all the added reagent remained in solution. This produced a striking improvement—the red colour now appearing instantaneously. This marked dependence of the rate of formation of the complex on the concentration of bathophenanthroline agrees qualitatively with the findings of Lee, Kolthoff and Leussing,[6] who have shown that the law governing the rate of formation of ferroin involves a third-power dependence on the concentration of phenanthrolinium ions.

Recoveries of added iron from the proposed base solutions were, however, not very satisfactory, since they are dependent on the amount of citrate present. The results are shown in Table I.

TABLE I

RECOVERY OF IRON FROM VARIOUS BASE SOLUTIONS

Base solution	Iron added, μg	Iron recovered, μg	Optical density at 533 mμ in 4-cm cell
Acetate	11·2	11·2	0·710
10 ml of a 50 per cent. solution of sodium citrate	11·2	10·3	0·650
25 ml of a 50 per cent. solution of sodium citrate	11·2	8·2	0·520

Trials with other complexing agents were carried out, but finally the most satisfactory was found to be a mixture of 20 ml of 0·1 M EDTA and 10 ml of a 50 per cent. solution of sodium citrate.

Recoveries of added iron were then carried out at various levels, both in the presence and absence of bismuth. The results are shown in Table II.

TABLE II

RECOVERY OF ADDED IRON BY THE PROPOSED METHOD

Bismuth present, g	Iron added, μg	Iron recovered, μg	Optical density at 533 mμ in 4-cm cell
	11·2	11·2	0·653
1	11·2	11·3	0·658
		11·2	0·654
		10·7	0·628
		11·6	0·683
1	5·6	5·8	0·342
		4·7	0·276
		4·9	0·286
1	1·1	1·4	0·085
		1·1	0·064
		1·4	0·082
		1·4	0·086
		1·1	0·062
		1·1	0·066

It can be seen that the optical density equivalent to 11·2 μg of iron is lower in Table II than it is for the experiment in an acetate base solution in Table I. This is because recoveries from the citrate base solution are reproducibly lower than those from the acetate base solution. If the calibration is prepared in the citrate solution, 100 per cent. relative recoveries will be obtained.

The above-mentioned differences in optical densities would no doubt disappear if the concentration of bathophenanthroline were increased to the point where a vanishingly small amount of iron[II] remained uncomplexed in acid solution. Since the free acidity of the bismuth solution must be 1 to 2 M to prevent precipitation of oxy salts, and since the complexing of iron[II] is dependent on the ratio of the concentration of reagent to hydrogen

ions, it is impracticable to attempt to achieve the concentration of reagent likely to be necessary.

The proposed method gives excellent results at all levels down to 1 μg of iron.   Levels below this can be determined, the limits being dependent on the magnitude and reproducibility of the blank value.

METHOD

REAGENTS—

All reagents should be of recognised analytical grade.   Redistilled or demineralised water should be used throughout.

Bathophenanthroline solution, 0·2 *per cent.*—Dissolve 0·5 g of 4 : 7-diphenyl-1 : 10-phenanthroline in 175 ml of ethanol.   Dilute to 250 ml with water and store in polythene.

Sodium citrate solution, 50 *per cent.* w/v.

EDTA solution—A 4 per cent. w/v solution of the disodium salt of ethylenediaminetetraacetic acid.

Stannous chloride solution—A 10 per cent. w/v solution of stannous chloride dihydrate.

Hydrochloric acid, concentrated, 6 M *and* 2 M.

Nitric acid, 16 M.

n-Hexyl alcohol.

Ethanol.

PROCEDURE—

Dissolve the bismuth in a mixture of 6 M hydrochloric acid and 16 M nitric acid (10 ml of hydrochloric acid and 0·5 ml of nitric acid per g of bismuth).   Evaporate the solution almost to dryness under an infra-red lamp.   Re-dissolve the solid in concentrated hydrochloric acid and repeat the evaporation.   Dissolve the residue in concentrated hydrochloric acid and dilute with water so that the solution contains 0·2 g of bismuth per ml and is approximately 2 M with respect to hydrochloric acid.   With a pipette, place 5 ml of the bismuth solution in a 10-ml beaker, add 0·2 ml of stannous chloride solution and boil.   Cool to room temperature and transfer the solution to a 100-ml separating funnel.   Rinse out the beaker with two 5-ml portions of ethanol, and finally with 2 ml of 2 M hydrochloric acid, transferring the washings to the funnel.

Add 4 ml of bathophenanthroline solution and mix thoroughly.   Mix 20 ml of EDTA solution with 10 ml of sodium citrate solution, and add it to the solution in the funnel, swirling to dissolve any precipitate formed.

Set the solution aside for 5 minutes and then extract the ferrous complex with 10 ml of *n*-hexyl alcohol.   Discard the aqueous phase and transfer the alcohol extract to a 25-ml calibrated flask, rinsing the funnel with ethanol.   Dilute almost to the mark with ethanol, add 0·2 ml of 2 M hydrochloric acid and shake until a clear solution is obtained.

Dilute to the mark with ethanol, filter the solution into a 4-cm cell and measure the optical density at 533 mμ.   Carry out a blank exactly as described above, but omitting the sample.

PROCEDURE FOR RECOVERING THE BATHOPHENANTHROLINE—

The present price of bathophenanthroline makes it desirable to recover it for further use, and this can be done as follows.   Evaporate the *n*-hexyl alcohol extract to dryness under reduced pressure.   Warm the residue with 10 N sodium hydroxide and then extract with hot benzene.   Evaporate the benzene; the residue should be fit to use again.

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The Determination of Trace Amounts of Lead and Bismuth in Cast Iron

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Trace amounts of lead and bismuth are separated from cast iron by extraction of the iron with *iso*butyl acetate from hydrochloric acid solution, and then by extraction of the lead and bismuth as their diethyldithiocarbamate complexes with chloroform from ammoniacal tartrate - cyanide solution. The lead and bismuth are then determined simultaneously with a cathode-ray polarograph, an acidified tartrate base electrolyte being used. The purification of the reagents is described.

BOTH lead and bismuth are rarely encountered in cast iron in other than trace amounts, almost invariably less than 0·1 per cent. and frequently less than 0·01 per cent. being present. At these concentrations the classical methods of separation, *e.g.*, of lead as sulphide,[1,2,3] are not satisfactory and at concentrations of less than 0·001 per cent. are completely inapplicable, even in the presence of carriers.[4,5]

The direct polarographic procedure[6] for lead in unalloyed steel and cast iron can be used for as little as 0·001 per cent. if a modern polarograph, such as the cathode-ray polarograph, is available, but it is open to interference by copper and tin. Most cast irons contain sufficient copper to interfere. For bismuth the direct iodide colorimetric procedure[7] is satisfactory down to about 0·01 per cent., but below this a preliminary separation becomes necessary.

Morrogh[8] and Dawson[9] have recently shown that very small amounts of various elements (titanium, lead, bismuth and antimony) have a markedly deleterious effect on the structure and physical properties of nodular-graphite cast iron. Their work has emphasised the need for accurate methods of determining these "subversive elements" at concentrations below 0·001 per cent. The work described in this paper has been carried out as part of the British Cast Iron Research Association's research programme in this field.

EXPERIMENTAL

It has been stated[10] that, in the presence of cyanide and tartrate at a pH of approximately 11, sodium diethyldithiocarbamate reacts only with lead, bismuth, thallium and cadmium. This statement was investigated with reference to the extraction of microgram amounts of both lead and bismuth from pure solutions. Final determination of the two elements was to be carried out simultaneously with the cathode-ray polarograph.

POLAROGRAPHY—

When 0·1 N hydrochloric acid was used as base electrolyte, it was not possible to determine less than 10 p.p.m. of bismuth in solution, owing to the severe distortion of the trace that occurs as the sweep passes through zero potential. The bismuth wave occurs at −0·15 volt* and is found on the steeply sloping part of the trace, which makes measurement impossible at low concentrations. In 0·1 N nitric acid, the wave is shifted to −0·35 volt, whereas the lead wave occurs at −0·75 volt. This bismuth wave, however, is closely followed by a large rounded wave, which has been attributed to the electro-capillary maximum.[11]

According to Lingane,[12] the most satisfactory base electrolyte for the simultaneous determination of lead and bismuth is a solution of sodium tartrate of pH 4 to 5. When a solution that was 0·1 N in nitric acid and approximately M in sodium tartrate (pH 4·5) was used, it was found that bismuth gave a very well defined wave at −0·45 volt and lead at −0·72 volt. Minor variations of pH resulted in slight shifting of these peak potentials, but had no apparent effect on the values of the peak current.

By using this base electrolyte, it was found possible to determine bismuth and lead down to as little as 0·02 p.p.m. When a 1-g sample and a final volume of solution of 5 ml are used, this corresponds to 0·00001 per cent., which was considered a satisfactory extension

* All potentials are given against the mercury-pool anode.

of the lower limit of determination for all samples, with the possible exception of very pure iron.

EXTRACTION—

Pure solutions of lead and bismuth were used and extraction was carried out from a solution containing 2 g of sodium tartrate, 1 g of potassium cyanide and 0·01 g of sodium diethyldithiocarbamate. The pH was adjusted to approximately 10 with ammonium hydroxide and the added lead and bismuth were extracted with chloroform. It was found to be most satisfactory to wash three times with chloroform, first with 15 ml and then with 10 and 5 ml. The chloroform extracts were transferred to a 50-ml beaker and evaporated to dryness, the organic residues were destroyed with nitric and perchloric acids and the excess of perchloric acid was removed by evaporating to dryness. The residues were dissolved in 1·0 ml of 5 per cent. nitric acid, 4·0 ml of sodium tartrate solution (200 g per litre) were added and the solution was transferred to the polarograph cell. With the lower range of concentrations, it was found to be necessary to de-oxygenate for at least 20 minutes. The oxygen step is never completely removed, but if it is sufficiently reduced the bismuth wave can be measured.

The results of this series of extractions were as follows—

Lead and bismuth added, μg of each	1000	100	10·0	1·0	0·1	0·05
Lead found, μg	1000	100	10·5*	1·4*	0·51*	0·50*
Bismuth found, μg	1000	100	9·8	0·97	0·11	0·04

* The blank value for lead in the reagents was 0·42 μg, but bismuth was not detected.

The reagents used for this series of determinations were purified as described later, p. 86.

As the results were satisfactory and since, under these conditions, the extraction is said to be nearly specific for lead and bismuth, a direct extraction procedure from a solution of a sample of iron was investigated. A 1-g sample of pure iron and some lead and bismuth were dissolved in dilute nitric acid, the iron was complexed with tartrate and, after the pH had been adjusted, traces of other metals, e.g., copper and nickel, were complexed with potassium cyanide. Sodium diethyldithiocarbamate was then added and the extraction was carried out as before. The results were extremely unsatisfactory; approximately 20 per cent. of both elements was recovered from each addition, the range of additions being the same as that used in the previous series of determinations.

In order to complex all the iron, it had been necessary to increase the amount of tartrate and the increased buffering action had necessitated the use of more ammonium hydroxide to attain the desired pH. A systematic investigation into the effect of the concentrations of tartrate, cyanide and diethyldithiocarbamate and the pH showed that none of the complexing agents had any deleterious effect when present in very large amounts. The effect of up to 20 g of tartrate and 5 g of cyanide in 100 ml of solution were investigated. Between pH 7 and pH 11 the recovery was quantitative.

It appears that ferric iron interferes in the extraction in some manner. A further series of additions and extractions was made, in which the iron was dissolved in hydrochloric acid and any ferric iron was reduced to ferrous iron with hydrazine dihydrochloride immediately before the extraction. The results were still very low.

The next series of additions was made to iron dissolved in aqua regia, and the bulk of the iron was removed by extraction with isobutyl acetate. Results were still low, and it was noticed that, after the addition of sodium diethyldithiocarbamate, the solution acquired a blue tinge. It was thought that this was due to ferro-ferricyanide formed by the reduction of some of the ferricyanide present by the diethyldithiocarbamate. This possibility was investigated further.

A further series of determinations was carried out with 4-g samples of pure iron, in which the residual iron present after the extraction with isobutyl acetate was reduced before extraction of the lead and bismuth. The results were very satisfactory and are shown in Table I.

It is apparent that reduction of the iron is necessary for complete extraction. When this is done, however, the extraction of bismuth under the conditions used is quantitative at least down to 0·1 μg, and the extraction of lead at least down to 3 μg.

It has been shown in our laboratory that, by using pure solutions of lead, the lead can be extracted quantitatively down to our lower limit of determination, i.e., 0·05 μg.

TABLE I

RECOVERY OF LEAD AND BISMUTH FROM PURE IRON

Lead and bismuth added to 4 g of pure iron, μg	Lead found, μg	Lead recovered, μg	Bismuth found, μg	Bismuth recovered, μg
Nil	3·7	—	0·18	—
0·1	3·7	—	0·29	0·11
1·0	4·7	1·0	1·2	1·02
10·0	13·5	9·8	10·2	10·0
100	117	113	98	98
1000	1030	1026	997	997

The effect of ferric iron on this extraction does not appear to have been reported previously in the literature. It is suggested that the effect is due to oxidation of the sodium diethyldithiocarbamate by ferric iron, when it is reasonable to assume that sulphide-type compounds are formed. These sulphide-type compounds would then react with lead and bismuth ions to form unionised compounds insoluble in chloroform, thereby removing them from the solution and preventing the extraction. Some support for this theory is given by the fact that the ferro-ferricyanide colour appears when sodium diethyldithiocarbamate is added to an ammoniacal tartrate - cyanide solution containing a small amount of ferric iron, but no ferrous iron. Further, on addition of the reagent a white turbidity similar to colloidal sulphur has been observed. Finally, solutions of sodium diethyldithiocarbamate on ageing for 24 hours deposit sulphur, and in this condition, as in the presence of ferric iron, the results are low.

By using the recommended procedure, a number of samples of iron were examined, and the results are shown in Table II. Corrections for the blank values of the reagents have been applied and the results show satisfactory reproducibility, even at the lowest levels investigated.

TABLE II

REPRODUCIBILITY OF RESULTS

Sample	Weight of sample taken, g	Lead found, %			Bismuth found, %		
Mild steel	1·0	0·0025,	0·0025		0·00004,	0·00005	
		0·0028,	0·0028		0·00002,	0·00002	
		0·0073,	0·0075, 0·0070		0·00071,	0·00076	
		0·0049,	0·0051, 0·0048		0·00002,	0·00003, 0·00003	
		0·0067,	0·0067, 0·0067		0·00001,	0·00002, 0·00002	
Pure iron	5·0	0·00019, 0·00019			0·000008, 0·000007		
Spectrographically pure iron	5·0	0·00009, 0·00009			0·000004, 0·000004		
Grey cast iron	4·0	0·00014, 0·00015			0·000006, 0·000007		
		0·00013, 0·00014			0·00015, 0·00015		

The extraction of cadmium and thallium was also investigated, but under the conditions used the recoveries were very low, probably owing to the high concentration of ammonium ions present. Recoveries varied from 10 to 60 per cent. of the amounts added.

As thallium and lead will give superimposed polarographic waves in acidified tartrate media, it is suggested that, if the presence of thallium is suspected, the lead should be determined in a sodium hydroxide base electrolyte. The cathode-ray polarograph will indicate the presence of thallium by giving a wave with a slight kink in the face of the peak, and will give a flat, or sometimes even a double-peak when the derivative circuit is used. Generally speaking, however, if thallium is present, it will have been added to the metal and its presence will therefore be suspected. None of the cast irons examined in our laboratory has been found to contain thallium, and cadmium has only been found at concentrations much lower than 0·0001 per cent.

INTERFERENCE—

The two major interfering elements in the direct polarographic determination of lead in iron are copper and tin. To check the effect of these elements, 0·05 g of copper and tin, and various amounts of lead and bismuth were added to a series of 1-g samples of pure iron. The lead and bismuth were determined and corrections were applied for the blank values of the reagents, the results being as follows—

Lead and bismuth added, μg of each	1000	100	10	1·0
Lead found, μg	1000	99	10	1·0
Bismuth found, μg	997	98	12	0·8

From these results it can be seen that there is little or no interference from these two elements.

No work was done on other alloying elements, but if the concentration of other elements is sufficiently low for them to be masked by the tartrate and cyanide, there should be no interference. It has been found that, with manganese contents greater than 1 per cent., a small amount of manganese is sometimes extracted. This has no effect on the polarographic determination, unless it is present as manganese dioxide, when it colours the final solution pale yellow to brown. Under these conditions, a wave from zero potential is obtained, but it is easily suppressed by adding 1 or 2 mg of hydrazine dihydrochloride or hydroxylamine hydrochloride.

METHOD

REAGENTS—

As the processing of up to 5 g of iron requires a considerable amount of reagents, the blank values are frequently so high that they render the results useless. The use of AnalaR reagents when available gave blank values of 25 μg of lead and 5 μg of bismuth. Steps were therefore taken to obtain reagents of a higher degree of purity. Nitric, hydrochloric and perchloric acids and ammonium hydroxide were originally distilled in order to purify them, but the reagents supplied as "lead free, for foodstuffs analysis" were found to be satisfactory, having lead contents of below 0·005 p.p.m.

Nitric acid, sp.gr. 1·42—"Lead free, for foodstuffs analysis."

Nitric acid, 5 per cent.—Dilute 50 ml of the nitric acid, sp.gr. 1·42, to 1 litre with water.

Hydrochloric acid, sp.gr. 1·18—"Lead free, for foodstuffs analysis."

Perchloric acid, sp.gr. 1·54—"Lead free, for foodstuffs analysis."

Ammonium hydroxide, sp.gr. 0·880—"Lead free, for foodstuffs analysis."

isoButyl acetate—Carry out a blank test on each bottle by shaking 100 ml of the reagent with 10·0 ml of 2 N nitric acid and determining the lead polarographically. When necessary, purify the reagent by shaking it with 2 N nitric acid and then with 5 N hydrochloric acid to remove most of the nitric acid and leave the reagent ready to extract ferric chloride.

Sodium tartrate solution, 200 g per litre—Dissolve 200 g of neutral sodium tartrate in 700 to 800 ml of water and shake with 50-ml portions of a 0·05 per cent. solution of dithizone in chloroform until there is no further colour change in the chloroform layer. Then shake the aqueous phase with chloroform until the extracts are colourless and remove the excess of chloroform by boiling. Cool and dilute the solution to 1 litre.

Potassium cyanide solution, 200 g per litre—Dissolve 200 g of potassium cyanide in 700 to 800 ml of water and add 10 ml of a 0·1 per cent. solution of sodium diethyldithiocarbamate. Extract the solution with three 50-ml portions of chloroform and then dilute to 1 litre. This solution must be freshly prepared.

Sodium diethyldithiocarbamate solution, 0·1 per cent.—Dissolve 0·1 g of the pure salt in 100 ml of water, add 2 or 3 drops of ammonium hydroxide, sp.gr. 0·880, and extract with two 10-ml portions of chloroform. This solution must be freshly prepared.

Chloroform—AnalaR chloroform has not been found to contain lead or bismuth. If the presence of these elements is suspected, shake the reagent with 2 N nitric acid and then wash it with water.

GENERAL REMARKS ON REAGENTS AND APPARATUS—

For lead contents down to approximately 0·0001 per cent. and bismuth contents down to approximately 0·00005 per cent., AnalaR acids and ammonium hydroxide will give satisfactory blank figures. The normal reagent grade *iso*butyl acetate rarely requires purification and AnalaR chloroform has never been found to be contaminated.

For all lead contents below 0·01 per cent., however, it is necessary to purify the tartrate and cyanide solutions as described. Distilled water is satisfactory in conjunction with AnalaR acids and ammonium hydroxide.

For lead contents below 0·0001 per cent. and bismuth below 0·00005 per cent., it is necessary to use the highest purity reagents as already described. Distilled water can be further purified by passing it through a mixed-bed de-ionising column. De-ionised water cannot, however, be used for the final solutions, as its use has been reported to cause difficulty with sensitive polarographs,[13] and our own experience confirms this. The sodium tartrate solution and the 5 per cent. nitric acid must be made up with distilled water and the polarograph cells must be rinsed with distilled water.

Apparatus must be scrupulously clean when used for the lower levels of lead and bismuth. Pyrex glass or a similar glass should be used for all apparatus, including cover-glasses. The use of soda-glass cover-glasses led to high and variable blank values.

Beakers must be covered and 2 N nitric acid boiled in them for 5 minutes before use, and they should then be thoroughly rinsed with distilled or de-ionised water. If apparatus can be reserved only for determinations of low concentrations of lead and bismuth, it will be found to give lower blank values after the first few determinations.

Removal of graphite and silica residues by filtration, with subsequent evaporation of the filtrates before extraction of the iron, was found to give high blank values. Filter-papers often contain microgram amounts of lead, which are difficult to remove by washing before use. For this reason, the silica and graphite residues in cast iron are removed after centrifugation.

MODIFICATIONS TO PROCEDURE—

The procedure should be modified to suit the iron under consideration, as follows—

(a) *For lead and bismuth contents down to* 0·0001 *per cent.*—Use a 1-g sample and AnalaR reagents. If the contents are greater than 0·01 per cent., a base electrolyte of 0·1 N nitric acid can be used, and the solution can be made up to 25 ml in a calibrated flask. However, a blank determination on all the reagents must be carried out.

(b) *For lead and bismuth contents below* 0·0001 *per cent. in normal irons and steels*—Use a 4-g sample and purified reagents.

(c) *For pure iron with low concentrations of manganese and other constituents*—Omit centrifugation and use the entire 5-g sample. Transfer the dissolved residue directly to the separating funnel, hydrochloric acid being used to assist the transfer. The volume of tartrate solution can be reduced to 5 ml and the cyanide solution to between 1 and 2 ml, and the solution made just ammoniacal before extraction of lead and bismuth. These modifications help to give a lower blank value.

(d) *For materials with low concentrations of silicon that do not contain graphite or other insoluble residues*—Omit centrifugation.

PROCEDURE—

Weigh 5 g of sample in a 400-ml squat beaker and dissolve it in 35 ml of hydrochloric acid and 10 ml of nitric acid, sp.gr. 1·42. When dissolved, evaporate to dryness, but do not allow the residue to bake. Dissolve the residue in 20 to 30 ml of hydrochloric acid, with gentle warming if necessary, and cool. By using hydrochloric acid contained in a polythene squeeze wash bottle as wash liquid, transfer the solution to a 100-ml calibrated flask (or direct to a separating funnel, see modification (c)). Dilute to the mark with hydrochloric acid and mix well.

Transfer the solution to a clean dry centrifuge tube and spin in a centrifuge at 3000 r.p.m. and 10-cm radius for 3 to 5 minutes. By means of a pipette, put either 20 ml (for the 1-g sample) or 80 ml (for the 4-g sample) into a pear-shaped separating funnel of suitable size and add *iso*butyl acetate (50 ml for the 1-g sample or 150 ml for the 4 or 5-g sample). Shake well, allow to separate and run off the acid phase into a 150-ml beaker. Evaporate just to dryness.

Dissolve the residue in 10 drops of hydrochloric acid and add 15 ml of water. Heat to between 80° and 90° C and add approximately 0·1 g of hydrazine dihydrochloride; maintain at 80° to 90° C for about 3 minutes in order to reduce all the iron, and then cool. Transfer the solution to a 150-ml pear-shaped separating funnel, using water to assist the transfer. Add 10 ml of sodium tartrate solution, 30 ml of ammonium hydroxide, 10 ml of potassium cyanide solution and 10 ml of sodium diethyldithiocarbamate solution, shaking the separating funnel after each addition.

Add 15 ml of chloroform, shake for 1 minute and allow the layers to separate. Run off the chloroform layer into a 50-ml beaker. Shake the aqueous layer with a 10-ml and then a 5-ml portion of chloroform and add these extracts to the contents of the beaker. If the lead or bismuth content is in excess of 0·01 per cent., use two 15-ml portions before the 10-ml and 5-ml portions and evaporate the earlier portions before adding the next.

Evaporate the combined chloroform extracts to dryness, remove the beaker from the hot-plate and add 2·0 ml of nitric acid, sp.gr. 1·42, and 2·0 ml of perchloric acid. With the beaker covered, evaporate gently to fumes of perchloric acid and continue until all the organic material is destroyed. Remove the cover and evaporate to dryness.

Cool and dissolve the residue in 1·0 ml of 5 per cent. nitric acid, added from either a 1-ml pipette or a semi-micro burette, and add 4·0 ml of sodium tartrate solution from a semi-micro burette. Transfer the solution to a polarograph cell and pass nitrogen through it for between 3 and 20 minutes depending upon the amount of lead and bismuth present. Record polarograms for bismuth, peak potential at −0·45 volt, and lead, peak potential at −0·72 volt, against the mercury-pool anode.

For the lower range of concentrations a cathode-ray polarograph will be required.

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A Micro Procedure for the Electrolytic Determination of Lead in Copper-base Alloys

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A study has been made of the conditions affecting the electrolytic deposition of micro amounts of lead as peroxide in copper-base alloys, particularly brass, by using a sample weight of 5 mg containing a maximum of 250 μg of lead. The significance of factors such as the time of the electrolysis, the temperature of the electrolyte and the presence of other alloying metals and impurities has been separately investigated.

It has been shown that, when the temperature of the electrolyte is 80° C and a potential difference of 2 volts is applied, reliable results can be obtained by using the specially designed micro apparatus with a platinum wire as anode, provided that manganese and arsenic are absent. In the presence of manganese the same method is applicable, but the temperature of the electrolyte must be maintained at 20° C. When arsenic is present, the results are slightly high.

MICRO procedures for determining lead by electro-deposition as peroxide have been published,[1,2] and the results given in the milligram range are satisfactory. Laboratories occasionally receive samples for analysis that involve the determination of lead in the microgram

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range, and, as far as is known, no results have been given for the accuracy of the electro-deposition procedure for these smaller amounts. With the object of developing a method that could be applied to 5 to 10-mg samples of copper-base alloys, particularly brasses containing about 3 per cent. of lead, a further study of this procedure was necessary.

EXPERIMENTAL

APPARATUS—

The modified Benedetti-Pichler type of micro electro-deposition[3] apparatus, shown in Fig. 1, was used for these experiments and losses on transference of the sample were avoided by weighing it in a small glass dish, which was then transferred to the electrolysis cell and remained there during dissolution of the sample and electrolysis. The electrolysis cell was a Pyrex-glass test-tube, $1 \cdot 6$ cm $\times$ $12 \cdot 5$ cm, and the receiver was a Pyrex-glass boiling-tube, $2 \cdot 5$ cm $\times$ $15 \cdot 5$ cm. A piece of No. 6 s.w.g. platinum wire was used as an anode, the lower end being wound in the form of a spiral. The cathode was a small platinum gauze cylinder, $2 \cdot 7$ cm $\times$ $1 \cdot 4$ cm, separated from the anode by a glass sleeve. Agitation was effected by gently passing a stream of air through a narrow syphon tube situated in the centre of the spiral anode. During weighing, the anode was counterpoised against a platinum wire of similar shape and weight.
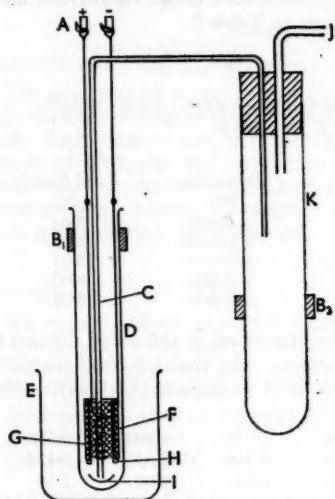

Fig. 1.   Apparatus for the micro electro-deposition of lead: A, platinum hooks on apparatus stand; B_1 and B_2, clamps; C, syphon tube; D, electrolysis cell; E, water bath; F, cathode; G, anode; H, glass sleeve; I, sample dish; J, air inlet and suction tube; K, receiver for electrolyte

Fig. 2(a).   Glass hook for transferring anode

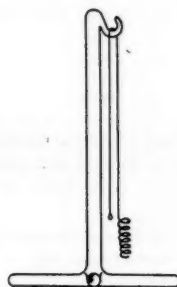Fig. 2(b).   Glass stand for suspending anode in oven or desiccator

TESTS ON STANDARD SOLUTIONS—

To test the efficiency of the electro-deposition procedure in the microgram range, a standard solution of high-purity lead in dilute nitric acid was prepared. By using a micro weight-burette, aliquots representing the lead content of 5 or 10-mg samples of brass were transferred to test-tubes, and copper nitrate solution was added to prevent cathodic deposition of lead. This combined solution was evaporated to dryness in a bath of glycerol and the residue was dissolved in 5 to 10 ml of 1 per cent. v/v nitric acid.

The conditions of electrolysis that were found to be suitable were (a) a temperature of about 80° C, (b) a potential difference of 2 volts, and (c) a current density of 8 mA per sq. cm. These conditions are similar to those applied by other workers.[1,2,4] After 10 minutes, the anode and the walls of the tube were washed with a jet of water and the electrolysis was

continued for a further 10 minutes. The anode containing the deposit was dried at 180° C, and, in calculating the results, a theoretical factor of 0·8662 was used. This factor was used throughout the experimental work. Recoveries from solutions containing known amounts of lead were as follows—

Lead present, mg	..	..	0·128	0·161	0·148
Lead found, mg	..	..	0·131	0·159	0·153
Difference, mg ..	..	..	+ 0·003	− 0·002	+ 0·005

The slight differences observed were due largely to weighing errors. For a 10-mg sample of brass containing 3 per cent. of lead, the greatest difference would be equivalent to about ± 0·05 per cent. of lead. Electrolysis at room temperature was equally satisfactory, but a total time of at least 40 minutes was necessary. No interference was observed from nitrous fumes formed during electrolysis and the possibility of retention of water by the very small deposit was ignored.

ANALYSIS OF LEADED BRASS—

A leaded brass ingot containing 2·93 per cent. of lead, determined as molybdate on the macro scale, was examined. The surface of the ingot was skimmed and fine drillings were taken from several positions. These were well mixed and a weighed amount was used for preparing a standard solution, portions of which were examined under conditions identical with those mentioned previously. The results are shown in Table I.

TABLE I

DETERMINATION OF LEAD IN SOLUTIONS OF A COPPER - ZINC - LEAD ALLOY CONTAINING 2·93 PER CENT. OF LEAD

Equivalent weight of alloy taken, mg	Lead present, mg	Lead found, mg	Difference, mg	Lead found, %
4·677	0·138	0·141	+ 0·003	3·02
5·057	0·149	0·152	+ 0·003	3·02
5·985	0·176	0·180	+ 0·004	3·01
3·775	0·111	0·116	+ 0·005	3·07
5·423	0·160	0·165	+ 0·005	3·03

Separate 5-mg portions of the mixed drillings were dissolved in 0·6 ml of diluted nitric acid (1 + 3) and the solutions were evaporated to dryness. The residues were dissolved in 1 per cent. v/v nitric acid and the solutions were examined as before, the results being as follows—

Weight of sample, mg ..	4·982	5·462	4·891	5·231	4·904	4·731
Lead found, mg ..	0·146	0·166	0·135	0·154	0·151	0·136
Lead found, % ..	2·94	3·04	2·76	2·95	3·07	2·86

The average of these results is 2·94 per cent., which agrees reasonably well with the accepted value obtained by a macro procedure. The variation in results is probably due to differences in the lead content of the small samples.

INFLUENCE OF IMPURITIES—

High results by the electro-deposition procedure have been reported by some workers and are attributed to the presence of other elements, notably manganese, bismuth, arsenic, antimony and phosphate; the influence of these elements was separately investigated. Because tin and silicon may be present in alloying amounts in some copper alloys, interference by these metals was also investigated.

INFLUENCE OF MANGANESE—

By using the electrolytic procedure, Tucker[5] obtained results that indicated that recovery of lead is almost quantitative provided that (a) copper ions are present, (b) the solution is cold at the beginning of the electrolysis, and (c) rapid deposition of lead is made from 5 to 10 per cent. v/v nitric acid. Tests were accordingly made to assess the effectiveness of this separation under various conditions of acidity, when only microgram amounts of lead are present, by using solutions prepared from high-purity lead, zinc, copper and manganese. The equivalent of 5-mg samples of brass containing 3 per cent. of lead and 3 per cent. of

manganese were electrolysed for 40 minutes at room temperature, *i.e.*, an initial period of 20 minutes and 20 minutes after washing the electrodes.   The results in Table II show that (*i*) 3 per cent. v/v nitric acid is suitable, (*ii*) lead is not deposited when the concentration of acid is increased to 10 per cent. v/v, (*iii*) manganese is not co-deposited with lead (manganese was not detected by a chemical test on one of the deposits), and (*iv*) all recoveries are as good as those obtained in the absence of manganese.   Further proof of the absence of interference by manganese at this concentration was obtained by analysing weighed amounts of drillings to which the equivalent of 3 per cent. of manganese had been added.

TABLE II

INFLUENCE OF MANGANESE ON THE DETERMINATION OF LEAD BY ELECTRO-
DEPOSITION AT 15° TO 20° C FOR 40 MINUTES

Concentration of nitric acid, % v/v	Manganese added, mg	Lead taken, mg	Weight of deposit calculated as lead, mg
10	0·150	0·164	Nil
3	0·150	0·150	0·152
3	0·150	0·153	0·153
3	0·150	0·162	0·156
3	0·150	0·158	0·155*

* Manganese was not detected in this deposit.

INFLUENCE OF OTHER ELEMENTS—

The presence of 1 per cent. of silicon and 0·1 per cent. of phosphorus (as phosphate) had little effect on the recovery of lead; 3 per cent. of tin and 0·1 per cent. of bismuth caused slightly high results and 0·1 per cent. of antimony caused slightly low results.   These amounts of bismuth and antimony, however, are greater than would be encountered in practice and only in the presence of arsenic were results unacceptable.   When co-deposition of other elements occurs, *e.g.*, arsenic, an alternative method for completing the determination of lead in the deposit must be used.

METHOD

REAGENTS—

Nitric acid, 25 per cent. v/v—Add 25 ml of nitric acid, sp.gr 1·42, to 75 ml of water.
Nitric acid, 1 per cent. v/v—Add 10 ml of nitric acid, sp.gr. 1·42, to 90 ml of water. Boil to remove nitrous fumes and make up to volume again with water.   For use, dilute 10 ml to 100 ml with water.
Hydrochloric acid, 50 per cent. v/v.
Potassium iodide.
Carbon tetrachloride.

PREPARATION OF THE APPARATUS—

Bend the upper portion of the anode to form a loop and suspend it by a glass hook (see Fig. 2) in a boiling-tube containing 50 per cent. v/v hydrochloric acid and a few crystals of potassium iodide.   Then wash the wire with a jet of water and suspend it on a glass hook in a drying oven maintained at 180° C.   After 15 minutes, transfer the anode to the hook of a glass stand in a desiccator (without desiccant) and allow it to stand for 5 minutes. Finally, transfer the anode to the pan of a microbalance and weigh it after 5 minutes; use an identical platinum wire as counterpoise.   Straighten the upper portion of the wire, pass it through the cleaned cathode and glass sleeve, already attached to the apparatus, and arrange the spiral over the lower portion of the air-supply tube.   Attach the anode to the positive terminal of the apparatus, already connected to a 2-volt accumulator, and gently pass a stream of air through the apparatus.

Note that, after removing the lead peroxide from the anode with the hydrochloric acid - potassium iodide solution and then washing, the bent portion of the stem should be heated in the flame of a bunsen burner to anneal it, thereby preventing early fracture.

PROCEDURE FOR PREPARING AND WEIGHING THE SAMPLE—

Use a drop of mineral oil at the position of sampling to prevent the drillings from scattering.

Lightly skim the surface with a small drill, a dental drill is suitable, and wipe the area clean.   Add a further drop of oil and continue to drill the cleaned area.   Transfer the drillings to a 2-ml centrifuge tube containing carbon tetrachloride, wash them about six times with the solvent, dry them at room temperature for 15 minutes and then remove any particles of iron with a magnet.

Prepare a small hemispherical glass dish having a diameter of between 10 and 15 mm and weighing about 0·3 g from the blown-out end of a sealed glass tube.   Clean the dish and dry it in an air oven.   Allow it to cool in a desiccator for 5 minutes, transfer it to the micro-balance and weigh after a further 5 minutes.   Introduce 5 to 10 mg of the prepared drillings and re-weigh.

PROCEDURE FOR DETERMINING LEAD—

Transfer the glass dish and sample by means of forceps to the mouth of the electrolysis cell, while holding the cell horizontally.   Raise the cell slowly to the vertical position so that the dish slides to the bottom and remains upright.   Add 0·6 ml of 25 per cent. v/v nitric acid by introducing a pipette into the cell until the tip is about $\frac{1}{2}$ inch from the glass dish, and then allow the acid to fill the dish to prevent it floating.   Allow the sample to dissolve and transfer the electrolysis cell to a bath of glycerol heated to 105° C.   Evaporate the solution to dryness by gently passing a stream of air filtered through cotton-wool in a glass tube having one end drawn out to a capillary.   Add 5 to 10 ml of 1 per cent. v/v nitric acid, i.e., only sufficient to cover the gauze cathode, rotating the tube during the addition to wash the walls of the tube.   Heat in a hot-water bath until all salts are dissolved.   For alloys containing manganese, dissolve the dried residue in 3 per cent. v/v nitric acid and proceed with the electrolysis at room temperature for a total time of 40 minutes.

Slide the test-tube up over the electrodes and, when they are almost touching the glass dish, clamp the test-tube in position.   Place a 100-ml squat-form beaker, containing water at 80° C, around the lower part of the   test-tube and maintain at this temperature with a microburner flame.   Electrolyse the solution for 10 minutes, and then wash the inner wall of the test-tube, the air-supply tube and the upper portion of the electrodes with a few millilitres of water.   Continue the electrolysis for a further 10 minutes.   Remove the hot-water bath and replace it by a beaker of cold water.   Disconnect the air supply and transfer the electro-lyte by gentle suction to the larger tube used as a receiver.   Half fill the electrolysis cell with water and continue agitation by passing air for a few seconds.   Remove the water bath and electrolysis cell.   Immediately disconnect the 2-volt supply and gently remove the anode. Bend the upper portion of the wire through 180°, suspend it on a glass hook and wash the entire length of the wire, including the spiral, by gentle application of a jet of water.

Place the anode on the glass stand in an air oven at 180° C for 15 minutes, transfer it to the desiccator and allow it to stand for 5 minutes, then to the microbalance for 5 minutes and then weigh.   Calculate the weight of lead deposited by multiplying the weight of lead peroxide deposited by 0·8662.

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The Micro-determination of Magnesium in Presence of Known Amounts of Calcium

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A method for the determination of magnesium in the range 0 to 1·0 μg in presence of between 0 and 5·0 μg of calcium has been developed with the use of a colour comparator. Calcium is determined with murexide as indicator and magnesium plus calcium, expressed as magnesium, with Eriochrome black T as indicator. The interference of calcium is much less than when ethylenediaminetetra-acetic acid is used. In twenty-one known mixtures of calcium and magnesium, the mean error of the results by the method was found to be 2·3 per cent. in the range −10 to +2 per cent. The method is applicable to the determination of calcium and magnesium in all proportions in organic solutions free from interfering ions and to deproteinised blood and cerebrospinal fluid, and its extreme simplicity makes possible multiple determinations of calcium and magnesium in small amounts in such fluids.

HUNTER and Stott[1] have described a micro method for the determination of magnesium in serum, in which the Eriochrome black T colour change is determined by using a new colour comparator. For the determination of magnesium in serum, the method has the chemical advantage of low affinity of calcium for the indicator compared with ethylenediaminetetra-acetic acid (EDTA), which titrates calcium and magnesium equivalently. In normal human blood plasma there are about 2·5 milli-equivalents of calcium and 0·8 milli-equivalents of magnesium per litre, so that rather more than 75 per cent. of the total EDTA titration is due to calcium, as contrasted with a corresponding value of about 15 per cent. in the method to be described. The most uncertain and time-consuming part of the method of Hunter and Stott is the removal of calcium with oxalate. Owing to the marked complexing action of oxalate, it is easy to introduce a greater error from this source than that due to the presence of the calcium.

It appeared that the removal of calcium might be unnecessary if it were possible to measure the magnesium equivalent of a known amount of calcium in the test portion used —known from a titration with murexide as indicator on a separate test portion. Since the colour comparator is sensitive to less than 0·01 μg of magnesium, it has been found to be possible to prepare a graph from which, after titration of mixtures of calcium and magnesium with a standard magnesium solution in presence of Eriochrome black T, the precise value for magnesium may be read. As the method has general application to mixtures of calcium and magnesium, and as it is both simple and time saving, the conditions for its success have been studied in some detail.

METHOD

APPARATUS—

The new colour comparator described by Stott,[2] which is being made available commercially by Messrs. Baird and Tatlock Ltd., was used. The comparator has two glass cups held vertically over a pair of barrier-layer photo cells, which are connected in series to a microammeter incorporating a transistor amplifier. Since the light beam is passed down the axis of the cups, the optical density is largely independent of dilution, and titration of the contents of one cup to match the other becomes possible. The titrant is delivered from a 5-ml burette, graduated in 0·01 ml, in approximately 0·01-ml drops, which pass through a slotted glass prism to avoid interference with the light beam. Provision is made for agitation of the cups.

REAGENTS—

All reagents must be prepared with water free from magnesium and calcium.

Calcium stock solution—Dissolve 250 mg of calcium carbonate in 5 ml of N hydrochloric acid, add 1 ml of 0·1 per cent. w/v solution of thiomersal (sodium ethylmercurithiosalicylate) and dilute with water to 100 ml.

$$1 \text{ ml} \equiv 1 \text{ mg of calcium.}$$

Calcium working solution—Dilute a portion of the calcium stock solution with water, so that—

$$1 \text{ ml} \equiv 10 \ \mu g \text{ of calcium.}$$

Murexide indicator solution—Dissolve 5 mg of ammonium purpurate in water and dilute to 250 ml. This reagent will keep for several days if stored cold in the dark.

Sodium hydroxide solution, N.

Magnesium stock solution—Dissolve 100 mg of magnesium ribbon in 9 ml of N hydrochloric acid, add 1 ml of 0·1 per cent. w/v solution of thiomersal and dilute with water to 100 ml.

$$1 \text{ ml} \equiv 1 \text{ mg of magnesium.}$$

Magnesium working solution—Dilute a portion of the magnesium stock solution with water, so that—

$$1 \text{ ml} \equiv 1 \ \mu g \text{ of magnesium.}$$

Eriochrome black T indicator solution A—Dissolve 100 mg of Eriochrome black T in 100 ml of methanol. Allow the solution to stand, with occasional shaking, for several days, then decant it from any inorganic residue and store it in a refrigerator.

Eriochrome black T indicator solution B—Dilute 10 ml of the indicator solution A to 100 ml with methanol.

Buffer solution—Mix 85 parts by volume of 1·5 M ammonium hydroxide with 15 parts of 1·5 M ammonium chloride. This solution has a pH of 10·25.

Buffer - indicator solution—Mix 10 ml of Eriochrome black T indicator solution B with 20 ml of the buffer solution and 20 ml of water. This solution, if cooled below 20° C, is usable for at least 1 hour.

PROCEDURE FOR DETERMINING CALCIUM—

To each cup of the comparator add 2·5 ml of murexide indicator solution and 0·3 ml of sodium hydroxide solution. Mix the solutions and adjust the pointer of the ammeter to zero with an Ilford No. 110 light filter in position. To the right-hand cup add a suitable volume of test solution, mix and add calcium working solution to the left-hand cup until the ammeter pointer returns to zero. The final volumes in the cups should be about equal; if they differ by more than 0·5 ml, a compensating volume of water should be added to the appropriate cup and the titration repeated. The amount of calcium present in the test portion is given directly by the burette reading.
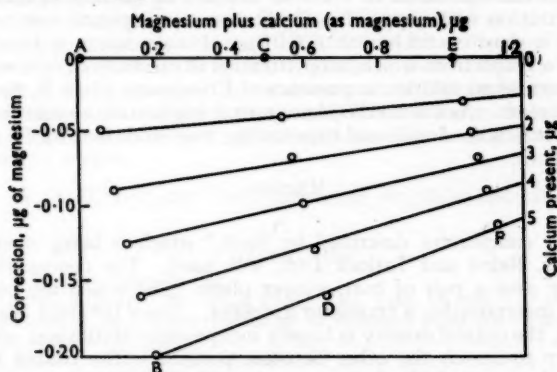

Fig. 1. Calibration graph for magnesium

PROCEDURE FOR DETERMINING MAGNESIUM PLUS CALCIUM—

To each cup of the comparator add 2·5 ml of buffer - indicator mixture. Set the ammeter to zero with an Ilford No. 204 light filter in position and add to the right-hand cup a suitable volume of test solution. Add magnesium working solution to the left-hand cup until the ammeter pointer returns to zero. The volume added from the burette is a measure of magnesium and calcium present in the test portion. The amount of calcium present in this is known from the titration with murexide as indicator and the magnesium present can then be read from a calibration graph such as that shown in Fig. 1.

PROCEDURE FOR PREPARING THE CALIBRATION GRAPH—

The calibration graph is an arbitrary construction dependent primarily on pH, but also affected by a number of other factors, such as concentration of indicator, ionic concentration and temperature. These factors are controllable within tolerable limits and values are reproducible with great precision. In the absence or presence of calcium there is a linear relationship between the titres and amounts of the metals present.

The calibration graph, shown in Fig. 1, was constructed as follows. Magnesium equivalents were determined, as described in the procedure for determining magnesium and calcium, in the absence of magnesium in the right-hand cup, for 1, 2, 3, 4 and 5 μg of calcium. This gave the series of points along line AB. A buffer - indicator mixture was prepared containing 0·5 μg of magnesium in 2·5 ml by mixing 10 ml of Eriochrome black T indicator solution B, 20 ml of buffer solution and 10 ml of magnesium working solution in a 50-ml calibrated flask and diluting to the mark with water. With 2·5 ml of this mixture in each cup, the pointer of the ammeter was adjusted to zero. From 1 to 5 μg of calcium were added to the right-hand cup as before and the left-hand cup was titrated with standard magnesium solution. By adding the readings to 0·5 μg, a series of points was plotted along line CD. Similarly, a buffer - indicator mixture was prepared containing 1·0 μg of magnesium in 2·5 ml and from 1 to 5 μg of calcium were added to the right hand cup and titrated as before. Again, by adding the titres to 1·0 μg, a series of points was plotted along line EF. Several intermediate magnesium levels have been checked and found to be linear with the values shown.

Similar calibration graphs have been prepared at pH values other than 10, with buffer solutions of different ionic concentrations and at different temperatures, and they were found to have similar linear relationships. The necessary observations for the construction of a calibration graph can be made in about 2 hours.

Examples of the use of the calibration graph—Let it be assumed that the magnesium plus calcium titre is 0·6 ml, or 0·6 μg as magnesium. Then if the test portion used contained 1 μg of calcium, a value of 0·04 μg has to be subtracted from the value for magnesium plus calcium, as magnesium, to give the true value of 0·56 μg of magnesium. If the test portion contained, successively, 2, 3, 4 and 5 μg of calcium, the values to be subtracted, corresponding to the same magnesium plus calcium titre as before, are 0·07, 0·10, 0·13 and 0·21 μg, which give true values of 0·53, 0·50, 0·47 and 0·39 μg of magnesium. Fractional values of calcium in the test portion can of course be readily interpolated.

RESULTS

As a test of the accuracy of the calibration graph, a series of twenty-one solutions containing known amounts of calcium and magnesium with ratios of calcium to magnesium ranging from 100 to 1 was prepared. The calcium in each solution was determined by the proposed method. The amounts found in 0·2 ml of test solution are shown in Table I. Triplicate determinations of magnesium plus calcium were carried out by the method on 0·2 ml of each solution (the test portion of blood filtrates we normally use), and the mean titration values were used to determine from the calibration graph the correction to be subtracted to give the true values of magnesium. The results are shown in Table I, and it can be seen from these results that the mean errors of the determinations of calcium and magnesium are 1·6 and 2·3 per cent., respectively.

DISCUSSION OF THE CONDITIONS OF THE METHOD

Schwarzenbach[3] notes that the metal indicators act as chelating agents in a way similar to the complexones, such as EDTA. Most analysts, however, have used EDTA with murexide as indicator for determining calcium or with Eriochrome black T as indicator for determining calcium plus magnesium. Smith[4] has described a method for determining magnesium in blood serum, after removal of calcium with oxalate, in which the change of colour of Eriochrome black T with magnesium is measured in an absorptiometer. The method described by Hunter and Stott[1] made use of the new colour comparator described earlier, p. 93.

The proposed method depends primarily on the accurate measurement of calcium in terms of magnesium in presence of various amounts of magnesium. It will be seen from Fig. 1 that the magnesium equivalent of calcium decreases as the amount of magnesium present increases.

TABLE I

DETERMINATIONS OF CALCIUM AND MAGNESIUM IN KNOWN MIXTURES

The test portions used for the determinations of calcium were of 0·2, 0·4 and 1·0 ml
for the solutions containing 5, 3 and 1 μg of calcium, respectively; 0·2-ml test portions
were used for all the determinations of magnesium plus calcium

Calcium present, μg	Calcium found, μg	Error, %	Magnesium present, μg	Magnesium found, μg	Error, %	Ratio of calcium to magnesium
5·0	5·00	0	0·05	0·045	−10	100
	5·00	0	0·10	0·100	0	50
	5·00	0	0·20	0·195	−3	25
	4·95	−1	0·40	0·385	−4	12·5
	5·05	+1	0·60	0·610	+2	8·3
	5·10	+2	0·80	0·805	+1	6·2
	5·00	0	1·00	1·015	+1	5·0
3·0	2·93	−2	0·05	0·050	0	60
	3·00	0	0·10	0·090	−10	30
	3·02	+1	0·20	0·190	−5	15
	2·97	−1	0·40	0·390	−3	7·5
	2·92	−3	0·60	0·585	−2	5·0
	3·05	+2	0·80	0·800	0	3·7
	3·00	0	1·00	1·000	0	3·0
1·0	0·96	−4	0·05	0·050	0	20
	1·02	+2	0·10	0·100	0	10
	0·98	−2	0·20	0·195	−3	5
	0·96	−4	0·40	0·400	0	2·5
	1·00	0	0·60	0·600	0	1·7
	0·98	−2	0·80	0·790	−1	1·2
	0·94	−6	1·00	1·000	0	1·0

Mean error of the determination of calcium = 1·6 per cent.
Mean error of the determination of magnesium = 2·3 per cent.

The method is suitable for the determination of calcium and magnesium in all proportions
in inorganic solutions free from interfering ions. It is probably applicable to most water
supplies. It has been used for over 2 years for the determination of calcium and magnesium
in blood and cerebrospinal fluids that have been deproteinised by the method of Hunter,[5]
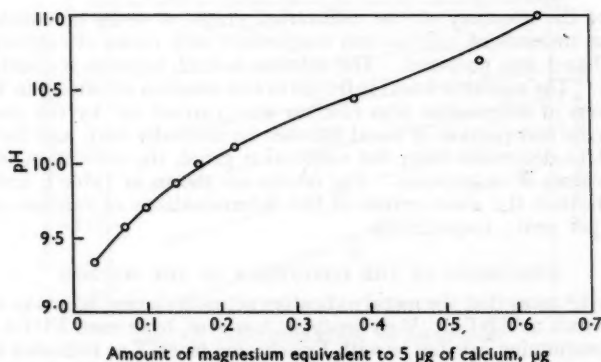and in the course of this work the main factors affecting its accuracy have been determined.

Fig. 2. Effect of pH on magnesium equivalent to 5 μg of calcium

Effect of pH—The effect of pH, at constant ionic concentration, on the magnesium
equivalent of 5 μg of calcium is clearly shown in Fig. 2, the magnesium equivalent rapidly
decreasing with pH. It might appear that at pH 9·0 calcium will not interfere at all, but
unfortunately the sensitivity of the determination of magnesium likewise decreases and the
end-point becomes uncertain below a pH of about 9·7. To keep a sharp end-point, a reaction
mixture of pH 10·0 has been chosen.

The change in the value of the magnesium equivalent of 5 μg of calcium with a small shift of pH might make the method appear to be impracticable. Yet this is not so. Relatively large amounts of acid are required to shift the pH appreciably.   For example, the addition of 0·2 ml of 0·1 N hydrochloric acid to 2·5 ml of the buffer - indicator mixture decreases the pH by less than 0·05 and the addition of 2 ml of blood filtrate (ten times the amount we normally use) has no measurable effect on the pH.   It may be noted that, in special circumstances, the buffering capacity can be doubled by mixing 1 part of indicator solution with 4 parts of buffer solution.

Concentration of indicator—The concentration of indicator in the buffer - indicator mixture, 20 μg per ml, is rather more than is necessary for the titration of 2 μg of magnesium. The choice of 5 μg of calcium to illustrate the effect of pH, concentration of indicator and ionic concentration was brought about by the appreciable magnesium equivalent titration obtained with this amount, although it is two to five times greater than the calcium present in the test portions used for the determinations of magnesium in blood and cerebrospinal fluid.

The effect of different concentrations of indicator was investigated by determining the magnesium equivalent of 5 μg of calcium with buffer - indicator solutions containing 20, 15 and 10 μg of indicator, the results being 0·21, 0·18 and 0·14 μg, respectively.   The concentration of indicator in the buffer - indicator mixture was decreased without changing the volume of methanol present or the ionic concentration of the mixture.   It can be seen from the results that decreasing the concentration of indicator decreases, as might be expected, the magnesium equivalent of calcium.   Dilution of the solution in one cup by 50 per cent. of its volume without changing the volume in the other cup introduces an error of about 15 per cent. with 5 μg of calcium.   Such differences in volume are extreme and the error would be less with less calcium, but for precise work, especially with large amounts of calcium, the volumes should be made approximately equal by adding water.

Ionic concentration—The effect of change in ionic concentration was investigated by determining the magnesium equivalent of 5 μg of calcium with buffer - indicator mixtures of ionic concentrations 1·2, 0·6 and 0·3 M, the results being 0·18, 0·20 and 0·23 μg, respectively. It can be seen that dilution of the 0·6 M mixture by 50 per cent. increases the magnesium equivalent of 5 μg calcium by about 7 per cent.   This is about half the effect of diluting the indicator, but it is in the opposite direction, so that the effects tend to compensate each other.

Effect of concentration of methanol—The buffer - indicator mixture contains 20 per cent. of methanol.   This has the effect of decreasing the pH of the buffer solution in the buffer - indicator mixture from 10·25 to 10·00.   Observations with different concentrations of methanol of from 2 to 42 per cent. indicate that changes in the magnesium equivalent of calcium over this range are attributable to changes in pH.

The presence of 20 per cent. of methanol has, however, the beneficial effect of sharpening the end-point of the titration of calcium - magnesium mixtures.   This has been noted by Betz and Noll.[6]

Effect of temperature—If the pointer of the ammeter is set at zero with 2·5 ml of buffer - indicator mixture in each cup and an equal volume of standard calcium solution is added to each cup, the pointer of the ammeter remains at zero at widely different temperatures, say, 15° and 25° C.   The same is true with an equal amount of magnesium added to each cup.   But if 5 μg of calcium are added to the right-hand cup and balance is achieved by adding magnesium to the left-hand cup at 15° C and the temperature is then changed to, say, 25° C, the ammeter indicates a slight over-titration.   With 5 μg of calcium alone, this temperature difference introduces a titration difference of about 10 per cent.   In presence of magnesium, the error is less and a scarcely perceptible difference was found between calibration graphs prepared at 17° and at 25° C.   A calibration graph prepared for a prevailing laboratory temperature would therefore appear to be valid to within ±5° C.

CONCLUSIONS

The foregoing experimental work deals primarily with the determination of magnesium in presence of calcium in simple solutions.   It is, however, indicated that deproteinised blood and cerebrospinal fluids may be regarded, for practical purposes, as such simple solutions, since the presence of phosphate, interfering metals and complexing agents such as citrate are negligible at the dilutions used.   However, the method is not yet directly applicable

to urine, owing to the presence of excess of phosphate, nor to ashed tissues, owing to interference from other metals such as iron.

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Rapid Methods of Boiler-water Analysis

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Methods are described for the rapid analysis of boiler-water samples, particularly those from high-pressure boilers. The total acidity of a sample that has been treated with a cation-exchange resin is found, after which the phosphate is determined by a simple titrimetric procedure. The chloride concentration is found by the oxycyanide method and the sulphate by difference. Possible interference is examined, and a method for the determination of sulphite is suggested.

WATER samples from high-pressure boilers (above 400 lb per sq. inch) and, in particular, power-plant boilers, usually contain only hydroxide, orthophosphate, sulphate, chloride and silicate, normally as their sodium salts. Sometimes, in plant working below 600 lb per sq. inch, sodium sulphite can be used as an oxygen scavenger and, in a few very isolated instances, tannins, often combined with hexametaphosphate, can be added. Tannins are, however, generally little used in high-pressure plant, and sulphite may even be deleterious.

Boiler-water analysis, therefore, consists in determining orthophosphate, sulphate, chloride and silica, hydroxide often being found by computation. This is a lengthy task when carried out by conventional analytical methods and some of the results may be of doubtful value. It appeared that a cation-exchange process could be usefully applied in the determination of at least some of the constituents of a normal boiler-water sample. Although apparently not widely applied in this country to boiler water, ion-exchange methods have been reported in another country.[1] It was also intended to examine and apply, if satisfactory, methods for phosphate and chloride determination not generally used in boiler-water analysis.

EXPERIMENTAL

CHLORIDE—

It has been customary in boiler-water analysis to determine chloride by the classical Mohr titration, after first suitably adjusting the pH value, but this method has been much criticised and its unsuitability is well known. It was considered that a more reliable method was required. Of the titrimetric methods available, that due to Vieböck[2] appeared most attractive. In this procedure, the neutralised sample is allowed to react with a solution of mercuric oxycyanide. The reaction involved is—

$$HgO.Hg(CN)_2 + 2NaCl + H_2O = HgCl_2 + Hg(CN)_2 + 2NaOH$$
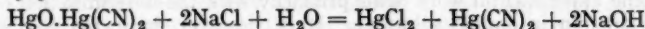
and the liberated sodium hydroxide is titrated with standard acid.

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In the routine analysis of boiler water, it is essential to determine the total alkalinity in order to determine later the sodium hydroxide concentration.   In our laboratory, alkalinity is determined by titration with 0·1 N sulphuric acid, B.D.H. "4·5" indicator being used. This appeared to be a convenient point at which to apply the Vieböck reaction, the liberated alkali being titrated to the end-point of B.D.H. "4·5" indicator.   Experimental work confirmed that chloride could be determined in this way.

Belcher, Macdonald and Nutten[3] have studied the Vieböck reaction and have found that it is not always stoicheiometric.   They have suggested applying a comparison titration procedure with a standard solution of sodium chloride.   This method was examined, but, despite its excellence, it was decided that the small errors involved in the present work did not justify the extra expenditure of time, and the direct titration was adopted.

Phosphate—

It is usual in boiler-water analysis to determine phosphate by one of the conventional methods depending on the formation of the molybdenum-blue colour.   Results are excellent when a photometric finish can be applied, but when visual comparison is necessary an alternative method would be valuable.

Töller[4] has suggested that for phosphate contents greater than 5 p.p.m. as P_2O_5 (approximately 10 p.p.m. as Na_3PO_4) the absorptiometric method is not sufficiently accurate and has suggested the use of a simple volumetric procedure.   In this, the phosphate is brought to the dihydrogen stage and sufficient silver nitrate is added to precipitate all the chloride and phosphate.   The phosphate reacts as follows—

$$NaH_2PO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3$$
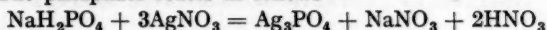
and the liberated nitric acid is titrated with standard alkali.

Previous work[5] had proved the accuracy and convenience of this procedure and originally the method was designed around this reaction.   More recently, however, a similar procedure has been described,[6] in which silver nitrate is replaced by cerous nitrate.   The mechanism is similar, but, since cerous chloride is soluble, the bulk of the precipitate formed is considerably less and end-points are much more distinct.

It was at this stage that an ion-exchange technique was applied.   In the phosphate determination it is immaterial whether the original solution is acid or alkaline, since it is brought to the dihydrogen phosphate stage, i.e., pH 4·5, before the reaction with cerous or silver nitrate.   By passing the boiler water through a small column of cation-exchange resin in the hydrogen form, the total acidity owing to the conversion of all the salts present to the corresponding acids could be found and used in the subsequent determination of sulphate.

The sample, after being treated with a cation-exchange resin, was boiled to remove carbon dioxide and then titrated with standard alkali to the end-point of methyl red - methylene blue indicator.   Excess of a neutralised cerous nitrate solution was added and the liberated nitric acid was titrated with 0·02 N alkali to the same end-point.   The original total-acidity titration was normally carried out with 0·1 N alkali, but, with samples of low dissolved-solids content, it was found preferable to use 0·02 N alkali.   When 0·1 N alkali was used, it was found advisable to add a drop of 0·1 N acid, and to adjust the end-point with 0·02 N alkali to guard against over-titration.   In all the titrimetric work described micro-burettes were used.

The results have been excellent with both silver and cerous nitrates.   Some slight difficulty was experienced in dealing with very low phosphate contents, particularly when silver nitrate was used, but this was readily overcome by first adding a known amount of a standard phosphate solution previously neutralised to methyl red - methylene blue indicator. The necessity for the addition of standard phosphate may readily be judged from the amount of colour change of the indicator after adding the silver or cerous nitrate solution.   With cerous nitrate solution the lower limit of phosphate determinable was considerably less than with silver nitrate and the results were good even with only 1 or 2 p.p.m. (as Na_3PO_4) present.

Because of its many advantages, the use of cerous nitrate has been adopted as routine practice.

Sulphate—

The conventional methods of determining sulphate in boiler water are the gravimetric barium sulphate method or the benzidine procedure with a volumetric finish.   The distinct

solubility of the precipitate renders the benzidine method of doubtful value.   In the presence of phosphate, the classical barium sulphate precipitation is open to considerable criticism. Previous work[5] had shown that the results are erratic and, in the present investigation, a barium sulphate precipitate was found to contain a considerable amount of phosphate.

In the proposed method, when the total acidity after cation exchange and the acidity equivalent to the chloride and phosphate by the Vieböck and cerous nitrate titrations, respectively, have been determined, the acidity equivalent to the sulphate, normally the only other anion present after ion exchange, may be found by difference.   (In this connection it must be remembered that, although two equivalents of nitric acid are liberated in the phosphate method, only one equivalent of the phosphoric acid formed by cation exchange is titrated.)

In order to assess the accuracy of the proposed methods, artificial boiler-water samples were prepared and analysed.   A sufficient range of composition was chosen to simulate conditions likely to arise in modern steam-raising practice.   Pure sodium chloride, disodium hydrogen phosphate and sodium sulphate were used in the preparation of the samples. The results are shown in Table I.   These results indicate that the methods are satisfactory over a wide range of boiler-water composition.   The figures for phosphate determination show that cerous nitrate yields somewhat better results than silver nitrate and it is considerably easier to find the correct end-point when cerous nitrate is used.

TABLE I

ANALYSIS OF SYNTHETIC BOILER-WATER SAMPLES

	Chloride, p.p.m. as NaCl—		Phosphate, p.p.m. as Na$_2$PO$_4$—			Sulphate, p.p.m. as Na$_2$SO$_4$—		
	present	found	present	found by—		present	found by—	
Sample No.				silver nitrate method	cerous nitrate method		silver nitrate method	cerous nitrate method
1	150	150	80	79	79	130	130	130
		150		78	80		133	133
2	100	100	5	4	5	100	104	100
		101		4	5		99	99
3	20	20	50	49	50	50	52	49
		19		50	50		50	51
4	20	20	20	19	19	20	22	22
		20		21	19		20	20
5	6	7	10	10	10	5	5	5
		7		8	9		4	4
6	20	19	80	79	80	20	19	20
		20		78	79		19	19
7	80	80	1	0	2	80	80	80
		81		0	2		82	81
8	50	50	5	4	5	100	103	102
		49		6	5		104	103
95 per cent. confidence limits		±1·5		±2·0	±1·4		±4·0	±3·0

METHOD

REAGENTS—

Sulphuric acid, 0·1 *and* 0·02 N.

Sodium hydroxide, 0·1 *and* 0·02 N.

Mercuric oxycyanide solution—Prepare a solution containing 20 g per litre.   Remove 10 ml and add to 50 ml of distilled water neutralised to B.D.H. "4·5" indicator.   Titrate this aliquot with 0·02 N sulphuric acid to the end-point of B.D.H. "4·5" indicator, using a micro-burette.   Now add the calculated volume of 0·02 N sulphuric acid to the remainder of the oxycyanide solution and mix thoroughly.   Test for neutrality by adding 10 ml to 50 ml of distilled water neutralised to B.D.H. "4·5" indicator.   No colour change should occur.   (This method of neutralisation is better than straightforward titration of the main solution, owing to the buffering action of mercuric oxycyanide.)

Cerous nitrate solution—Dissolve 25 g of cerous nitrate free from other rare-earth metals in distilled water.   Neutralise to methyl red - methylene blue indicator and dilute to 1 litre.

Methyl red - methylene blue indicator—Dissolve 0·125 g of methyl red in 50 ml of ethanol; dissolve 0·083 g of methylene blue in 50 ml of ethanol.   Mix equal volumes of these solutions.

PROCEDURE FOR DETERMINING CHLORIDE—

Titrate a 50-ml sample of boiler water with 0·1 N sulphuric acid (or 0·02 N if the alkalinity is low) to the end-point of B.D.H. "4·5" indicator.

Add 10 ml of neutralised mercuric oxycyanide solution and mix well.   Titrate with 0·1 or 0·02 N sulphuric acid to the same end-point as before.   The volume of 0·1 N sulphuric acid, in ml, multiplied by 117 (or 23·4 for the 0·02 N acid) gives the concentration of chloride, as p.p.m. of NaCl.

PROCEDURE FOR DETERMINING TOTAL ACIDITY AND PHOSPHATE—

Pass the boiler water through a column of Zeo-Karb 225 resin (hydrogen form), approximately 20 cm $\times$ 1·5 cm.   Reject the first 20 to 30 ml of effluent and collect 50 ml over a period of 2 to 3 minutes.   Boil the effluent to remove carbon dioxide (and sulphur dioxide if sulphite is present), cool and add methyl red - methylene blue indicator.   By using a micro-burette, titrate with 0·1 N sodium hydroxide (or 0·02 N if a small titre is expected).   This gives the total acidity.   If 0·1 N sodium hydroxide is used, add a drop of 0·1 N sulphuric acid after the total acidity has been determined and adjust the end-point with 0·02 N sodium hydroxide before proceeding with the phosphate titration.

Add 5 ml of cerous nitrate solution, mix well and titrate to the same end-point with 0·02 N sodium hydroxide.   The volume of 0·02 N sodium hydroxide, in ml, multiplied by 32·8 gives the concentration of phosphate, as p.p.m. of Na_3PO_4.

CALCULATION OF THE SULPHATE CONTENT—

Convert the total acidity and chloride titrations to the equivalent volumes of 0·02 N acid, then—

$$[A - (C + 0·5\,P)] \times 28·4 \equiv \text{amount of sulphate, as p.p.m. of } Na_2SO_4,$$

where A = volume of 0·02 N sodium hydroxide, in ml, used for total acidity,

C = volume of 0·02 N sulphuric acid, in ml, used for chloride, and

P = volume of 0·02 N sodium hydroxide, in ml, used for phosphate.

POSSIBLE INTERFERENCES IN THE METHOD

Of the constituents found in boiler water apart from those already mentioned, only silicate, nitrate, sulphite and tannin will appear in amounts likely to affect the determination under consideration.

Silicate is present in boiler water in amounts ranging from 1 or 2 to between 20 and 30 p.p.m. (as SiO_2), and, especially at pressures exceeding 600 lb per sq. inch, its ingress is closely controlled.   In the present series of experiments, up to 20 p.p.m. of SiO_2 had no deleterious effect.

The presence of nitrate in a high-pressure boiler arises only from contamination by cooling water and the nitrate content is unlikely to rise above a few parts per million.   Such amounts are of no operational consequence, and would be calculated as sulphate.   Should nitrate be present in significant amounts, it would have to be determined separately and its equivalent acidity deducted from the acidity equivalent to the sulphate.   A method for the titrimetric determination of nitrate has been proposed by Ungar.[7]

As indicated earlier, the use of sulphite has largely disappeared, but it is employed in some units that work below 600 lb per sq. inch.   It is normal in these waters to add 10 p.p.m. of sulphite (as Na_2SO_3), but amounts up to 50 p.p.m. are not unknown.   No sulphite is used in our boilers, but it was deemed advisable to investigate its effect.

There is no interference from sulphite in the determination of phosphate, since, after cation exchange and boiling, sulphur dioxide is expelled.   In the Vieböck chloride method up to 50 p.p.m. of sodium sulphite had no ill effect.

During the period in which the methods above were being examined by other Divisions of the C.E.A., it was reported[8] that, for a boiler in which a proprietary compound consisting

of tannin and sodium hexametaphosphate (Alfloc "28" powder) was used, the results were very erratic when the original Töller method[4] was applied.

This was, in fact, found to be so. The tannin interference can, however, be removed by treating the sample with charcoal free from inorganic impurities. The boiler-water sample is then filtered and passed through the column of Zeo-Karb 225, and the total acidity and phosphate are determined by the proposed method. Tannins do not interfere in the Vieböck chloride method.

The sodium hexametaphosphate present in the Alfloc "28" powder is, under boiler operating conditions, rapidly hydrolysed to orthophosphate and is therefore included in the phosphate determination.

DISCUSSION

The method as outlined has been used successfully in the authors' laboratory for many months. It has yielded excellent results, which relate to operational practice more closely than when conventional methods were used.

It is found convenient to use a set of four columns. When a sample has been dealt with on a column, it is found that the rejection of the first 20 to 30 ml of the subsequent sample provides sufficiently thorough rinsing of the column. The frequency of regeneration of the columns with dilute acid is a matter of experience and depends on the salt concentration of the water samples.

The saving in time over the conventional methods is substantial. One ion-exchange process and four simple titrations enable all except the silica and sodium hydroxide concentrations to be determined, compared with the more laborious processes of dealing separately with each ion by titrimetric, colorimetric or gravimetric methods.

We have found a Kipp tilt-measure of appropriate capacity excellent for addition of the mercuric oxycyanide and cerous nitrate solutions, the volumes of which need not be exact.

Although the use of silver nitrate for phosphate has been abandoned, it still yields good results. It is used in the same concentration as cerous nitrate.

SUGGESTED METHOD FOR SULPHITE

Neutralise a 50-ml sample of boiler water to thymol blue - phenolphthalein indicator. Add a solution of formaldehyde (2 g per 100 ml) neutralised to the same indicator. Titrate the resulting alkaline solution with $0.02 N$ acid to the same end-point. The volume of $0.02 N$ acid, in ml, multiplied by 50.4 gives the concentration of sulphite, as p.p.m. of Na_2SO_3.

As previously stated, sulphite is not used in our boilers, but the results with synthetic solutions are encouraging.

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o-Dithiols in Analysis

Part VI.*   Diacetyltoluene - 3 : 4 - dithiol as a Coagulant, Catalyst and Precipitant for Sulphur and Metallic Sulphides

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When toluene-3:4-dithiol, or diacetyltoluene-3:4-dithiol, is added to a suspension of sulphides formed in acid solution, coagulation is hastened and the precipitated sulphides become water-repellent. Of the various sulphur compounds tried, none was as effective as these.   Diacetyltoluene-3:4-dithiol is more stable and less easily lost by volatilisation than toluene-3:4-dithiol. Addition of a trace of diacetyltoluene-3:4-dithiol to solutions before precipitation of group 2 cations as the sulphides improves coagulation, and the reagent acts as a catalyst for the decomposition of arsenates and molybdates. Tungsten is not precipitated as the sulphide, but excess of diacetyltoluene-3:4-dithiol precipitates tungsten as a complex that is soluble in alkali.   In presence of silicate the precipitation of tungsten is incomplete.   The addition of traces of diacetyltoluene-3:4-dithiol in ethanolic solution during precipitations of group 2 cations is recommended.   This reagent is also a coagulant for colloidal sulphur in acid solution.

SINCE toluene-3:4-dithiol (dithiol) often displaces hydrogen sulphide from metallic sulphides,[1,2] it was thought that its addition to an aqueous suspension of an insoluble sulphide might coat the particles of the sulphide with a layer of strongly lyophobic mercaptide, and so aid coagulation.

Experiment at once confirmed this expectation.   Dithiol was found to be a powerful coagulant for sulphide precipitates in acid solutions, and in no instance was interference to the usual procedure of dissolution and separation of the sulphides noted.   The presence of a lyophobic surface on particles of sulphides was easily shown by the following experiment. A mixture of all the more common group 2 cations was precipitated by hydrogen sulphide under the usual analytical conditions and a trace of ethanolic dithiol was added.   By adding ethylene dichloride or benzene, with shaking, the precipitate entered immediately and entirely into the organic layer.   In absence of dithiol, however, it remained in the aqueous layer or collected at the interface.

Experiments were then conducted with other sulphur-containing compounds.   A solution of arsenious sulphide prepared by saturating 100 ml of a hot 2 per cent. solution of gum arabic containing 0·1 g of arsenious oxide with hydrogen sulphide was used.   To 2 ml of the solution in a test-tube, 0·4 ml of 2 N hydrochloric acid and a trace of the sulphur compound dissolved in 1 drop of ethanol were added.   The test-tube was heated in a water bath and the solution was compared with a blank solution at intervals during a period of 20 minutes.   In many tests comparisons were also made by passing hydrogen sulphide through 0·35 N hydrochloric acid containing all the more common cations (a precipitate of silver chloride also being present) and noting whether complete clarification occurred within 1 to 2 minutes.

The sulphur compounds found to be either inactive or only slightly active relative to dithiol were S-benzyl*iso*thiouronium chloride, 1-o-carbomethoxy-4-phenylthiosemicarbazide, diphenylthiocarbazide, *sym.*-diphenylthiourea, *m*-mercaptobenzoic acid disulphide, methylene blue, phenylthiourea, sodium diethyldithiocarbamate, sodium toluene-*p*-sulphinate, thioacetamide, thiosalicylic acid and thiourea.

1:8-Dimercaptonaphthalene,[3,4] quinoxaline-2:3-dithiol[5] and dibenzoyltoluene-3:4-dithiol (dibenzoyldithiol)[6] showed considerable activity, although less than that of dithiol.   Dithiooxamide exhibited a remarkable power of precipitating arsenious sulphide from solution, far surpassing that of dithiol, although, in general, it is inferior to dithiol—it does not cause precipitates to be wetted by benzene, sulphide precipitates formed in its presence are bulky, it does not catalyse the decomposition of arsenates and it does not precipitate tungstates (see later, p. 105).

* For details of previous parts of this series, see reference list, p. 106.

Diacetyltoluene-3:4-dithiol (diacetyldithiol)[6] was fully as active as dithiol, especially in acid solutions, and had the great advantage that, once added to a solution, it was much less readily destroyed or lost by volatilisation. In addition, it does not give rise to highly coloured compounds with, for example, molybdenum and tungsten, as does dithiol.

DIACETYLDITHIOL AS A COAGULANT FOR SULPHUR AND SULPHIDE PRECIPITATES

Diacetyldithiol was found to be a powerful coagulant even in presence of 1 per cent. solutions of starch, Teepol, gum arabic and similar materials. In one experiment, 10 ml of a solution containing about 0·2 per cent. of each of the salts of all the more common cations, 1 per cent. of arsenious oxide and 1 per cent. of gum arabic was made 0·3 to 0·4 N with respect to hydrochloric acid, the permanent precipitate formed being ignored. The mixture was heated and hydrogen sulphide was passed through. Much colloidal sulphide remained after 20 minutes. An exactly similar mixture containing 1 drop of 1 per cent. ethanolic diacetyldithiol became completely clear in 10 minutes. Coagulation could not, however, be effected in presence of 5 per cent. of gum arabic.

A trace of diacetyldithiol can be used with advantage in the course of ordinary qualitative analysis, when it causes an almost immediate coagulation of the sulphides of the group 2 metals. The sulphides of the more common group 2A metals usually separate so effectively that the supernatant liquid can be removed with the aid of a dropper without the need for filtration or centrifugation. Group 2B sulphides also coagulate rapidly, but are more bulky.

PRECIPITATION OF SULPHUR—

Diacetyldithiol, like dithiol, was also found to be a useful coagulant for elemental sulphur. A hot 1 per cent. acidified solution of sodium thiosulphate deposited its sulphur completely and in easily filterable form within 6 minutes when a trace of the reagent was added. No noticeable coagulation was observed with selenium in acid solution or with sulphur or sulphides in alkaline solution.

DIACETYLDITHIOL AS A CATALYST FOR PRECIPITATION OF ARSENIC AND MOLYBDENUM SULPHIDES

REDUCTION OF ARSENATE—

When dithiol or diacetyldithiol was added to a hot solution of an arsenate in dilute acid and hydrogen sulphide was passed through, or thioacetamide was added, the yellow colour of arsenious sulphide appeared earlier than usual and complete precipitation was speeded up (see Table I).

TABLE I

EFFECT OF ADDING CATALYSTS TO ACIDIFIED ARSENATE SOLUTIONS IN PRESENCE OF HYDROGEN SULPHIDE

Experiment	Time to first appearance of bright yellow precipitate, seconds	Time for complete precipitation of arsenious sulphide, minutes
(a) 10 ml of a 0·5 per cent. solution of arsenic oxide in 0·35 N hydrochloric acid were heated to boiling in a water bath and hydrogen sulphide was passed through briskly	90	15 or more
(b) As for (a), but with a trace of zinc dithiol sprinkled on the surface 2 or 3 times during precipitation ..	40	6
(c) As for (a), but with one drop of a 1 per cent. solution of diacetyldithiol added	35 to 40	6

In these and similar experiments it appeared likely that the reagents were acting as catalysts to promote reduction by hydrogen sulphide. In support of this view it was found that other reducing agents could sometimes be substituted for hydrogen sulphide. Thus, when excess of stannous chloride was added to hot 3 to 4 N hydrochloric acid containing much arsenic[V], no change was observed. When, however, a trace of the zinc complex of toluene-3:4-dithiol (zinc dithiol) or diacetyldithiol was added, the solution rapidly became red and metallic arsenic was soon precipitated.

PRECIPITATION OF MOLYBDENUM[VI]—

Molybdenum[VI], 0·003 to 0·03 M, in hot 0·3 to 0·4 N hydrochloric acid rapidly gave a precipitate resembling molybdenum sulphide when thioacetamide and a trace of diacetyldithiol were added.   The filtrate was colourless and free from molybdenum after 3 to 5 minutes.   When hydrogen sulphide was used, coagulation was rather less rapid.   The usual blue colloid was not formed and the filtrate was colourless and practically free from molybdenum (it gave a very pale yellow, but no green colour on treatment with zinc dithiol) in 4 to 6 minutes.   The presence of the more common group 2 metals did not interfere with the precipitation.

In hot 0·3 to 0·4 N hydrochloric acid containing molybdenum[VI], it was found that the development of colour (blue, yellow or pink) due to the reduction of molybdenum[VI] was markedly catalysed by the addition of a trace of diacetyldithiol.   The effect was observed with phosphorous acid, hypophosphorous acid mixed with phosphorous acid (reduction with hypophosphorous acid alone was too rapid for observations to be made), hydrazine, paraformaldehyde and formic acid.

When blue solutions were formed in absence of a catalyst, they were found to be unstable or much less stable than when the catalyst was added, and a dark precipitate always formed rapidly.   The effect was observed with phosphorous acid, hypophosphorous acid, hexamethylenetetramine, paraformaldehyde, hydriodic acid and hydroxylamine, as well as with hydrogen sulphide.

DIACETYLDITHIOL AS A PRECIPITANT FOR TUNGSTEN[VI]

On addition of diacetyldithiol to hot 0·3 to 0·4 N hydrochloric acid containing tungsten[VI], *e.g.*, 0·1 to 1 per cent. of sodium tungstate, a brick-red precipitate of low colour intensity, previously overlooked,[6] forms slowly and coagulates readily.   After 5 to 8 minutes the filtrate is free from tungstate.   Large excesses of phosphate, borate and tartrate, present together, do not interfere, and the appearance and properties of the precipitate are unchanged if hydrogen sulphide is also passed into the solution, or if thioacetamide is added.   The precipitate mainly dissolves in warm 2 N potassium hydroxide, leaving a little oily organic matter free from tungsten.   The alkaline extract gives a strong tungstate reaction with zinc dithiol and excess of hydrochloric acid.[7]   When excess of silicate was present, in addition to phosphate, borate and tartrate, the reaction was similar, but tungsten was not completely removed from the solution.   With a similar mixture acidified to 5 to 6 N with hydrochloric acid, the addition of diacetyldithiol resulted in the slow formation (15 to 25 minutes) of a bulky green precipitate, probably consisting mainly of silica, but a trace of tungstate still remained in the filtrate.

In 0·3 to 0·4 N hydrochloric acid, with tungstate and excess of phosphate present, dibenzoyldithiol gave a brick-red precipitate in 20 to 30 minutes, but in the presence of silicate no coloured product was formed within 3 hours.

DISCUSSION

It is of interest that the compounds found to function as highly reactive coagulants for sulphides in acid solution are all such as are capable of chelating with thiophilic atoms to form heterocyclic rings containing two sulphur atoms.

The results described would appear to indicate that diacetyldithiol is a useful analytical reagent (*a*) for the coagulation of sulphides in acid solution, (*b*) as a coagulant for sulphur in acid solution, (*c*) as a catalyst for the reduction of arsenates and molybdates in presence of hydrogen sulphide and their subsequent rapid precipitation as sulphides, and (*d*) as a precipitant for tungsten[VI] in dilute acid solution in the absence of silicate.   Its reactions with some rarer cations have previously been described.[6]

METHOD OF USING DIACETYLDITHIOL IN ANALYSIS

REAGENT—

Diacetyldithiol solution—Dissolve 1 to 5 mg of diacetyldithiol in 0·5 ml of 95 per cent. ethanol.

PROCEDURE—

Precipitation of group 2 cations by hydrogen sulphide—Adjust the acidity of the solution to 0·3 to 0·4 N with hydrochloric acid and heat to boiling.   Add one drop of diacetyldithiol solution and either pass hydrogen sulphide through or add thioacetamide.

Coagulation of the sulphides is usually extremely rapid and it is often possible to determine when precipitation is complete by passing hydrogen sulphide into the clear supernatant liquid.   Finally, add one more drop of reagent and boil to remove ethanol (see Note).   Filter or spin in a centrifuge and proceed as usual.

If the final addition of the reagent gives rise to a coloured precipitate within 1 minute, tungstate is probably present.   Add diacetyldithiol in excess and boil to complete the precipitation.

Precipitation of sulphur—Acidify the solution and add one drop of reagent.   Maintain at the boiling-point, adding more reagent if necessary until precipitation is complete.

Note—As diacetyldithiol is slightly soluble in hot dilute ethanol, the ethanol is removed by boiling, otherwise an excess may separate on cooling and cause a faint white turbidity.

I express my gratitude to Professor H. J. Eméleus, Mr. P. S. Jewell and Dr. F. G. Mann for their interest, and to Hopkin & Williams Limited for a gift of chemicals.

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Note—References 1, 2 and 6 are to Parts I, III and IV, respectively, of this series.

Composite Absorptiometry for the Control Laboratory

Examination of Calculating Procedures and Modification of the Spekker Absorptiometer for Use with Interference Filters

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Attempts are being made to adapt composite spectrophotometric procedures for use in control laboratories and two essential preliminaries to this work are described.

Graphical methods of solving simultaneous equations have been studied, and a triangular net and a "slide-rule" method have been examined practically.

The Spekker absorptiometer has been modified to permit the use of a more powerful tungsten-filament lamp as the light source.   The characteristics of some commercially available interference filters have been determined and their use in absorptiometry is discussed.

DESPITE the advent of quantometry in metallurgical control, it does not satisfy the demands of all laboratories and, when the application of chemical analytical procedures is still essential, the use of absorptiometry to speed up control methods is now well established.   When pelleted reagents are used in these methods, a great deal of the time and chemical skill required is reduced, and so the economy of the work is enhanced.   These absorption methods are generally monocolour and require either a separate sample or an aliquot, removed by means of a pipette from a master solution of the alloy, for each item determined.

In recent years in academic and research laboratories, spectrophotometric methods have been evolved for binary[1] and ternary[2] coloured systems.   In these, a mixed colour that is additive for the various coloured ions produced is developed, the assumption being made that there are no chemical interactions.   This mixed colour can be analysed into its *n* components by monochromatic measurements at *n* wavelengths at which the relative transmission coefficients of the separate species are already determinant.   The purity of the light

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used for these measurements must be of a high order, as the theoretical additivity of Beer's law only holds for monochromatic light. Given such purity in a spectrophotometer, these methods have proved satisfactory and have also been used in differential procedures in which standard coloured solutions are used as blanks.[3] Differential methods will not be dealt with here, as, although of high precision, they are necessarily time-consuming and unsuitable for the control laboratory except in limited circumstances.

GENERAL AIMS—

The use of multi-component systems in which the chemical pre-treatment of the samples can be minimised could obviously be of advantage in the control laboratory, to give two determinations for the price of one. However, in view of the final goal of simple rapid methods, the following limitations must be made—

(i) they should be capable of operation by semi-skilled staff and accordingly must have simple calculations that do not involve simultaneous equations,

(ii) the apparatus required should be simple, reliable and not too expensive (although capital outlay may well be offset rapidly by reduced running costs),

(iii) the procedures should be more rapid than the individual monocolour methods they replace, and

(iv) the ultimate scope of the procedures should be as wide as possible and free from interferences by other components normally found in the base material studied.

It is intended that practical applications of these procedures as applied to metallurgical inspection should be the subject of later communications from this laboratory. The present purpose is to describe work on two of the essential preliminaries as indicated above, *viz.*—

(a) an investigation of the graphical methods available for the solution of the simultaneous equations in two or more variables, and

(b) an investigation into the possibilities of converting the Spekker photo-electric absorptiometer for use in these procedures by using interference filters.[4]

GRAPHICAL SOLUTION OF SIMULTANEOUS EQUATIONS

BINARY SYSTEMS—

Simple four-scale parallel nomograms[5] can readily be drawn for the solution of this problem; they will have direct-reading scales for concentrations $[A]$ and $[B]$ with setting from optical-density scales D_1 and D_2 (where D_1 and D_2 are measured optical densities at wavelengths λ_1 and λ_2, and A and B are coloured components to be determined with absorption maxima at λ_1 and λ_2, respectively). A nomograph, however, is not precise and physiological problems arise when its size is increased to give scale accuracy. When the two setting scales are so far apart that they cannot be viewed simultaneously, any setting of the straight edge becomes a series of approximations as each point in turn is adjusted. Further, any mechanical setting errors are reflected in the result, possibly magnified. The nomograph is not amenable to reproduction by any procedure in which there is the possibility of paper shrinkage, which may not be uniform.

A triangular net, previously described,[6] has been in use for some years and, as it has proved sufficiently reliable and amenable to its semi-skilled users, it is put forward again. The original problem was not connected with absorptiometric methods or simultaneous equations, but the same principle is applicable.

Although it requires high-quality draughtsmanship in preparation, a net can be reproduced by any method without impairing its accuracy. From the theoretical standpoint the accuracy should be high, as no physical alignments are required: only a point has to be visualised relative to a small triangle as co-ordinates.

For the solution of the simultaneous equations arising in the present problem, two inter-related triangles are required to give the solutions—

$$[A] = CD_1 - C'D_2$$
$$[B] = C''D_2 - C'''[A]$$

Space can be conserved when the variables have specified ranges by drawing only part of the triangles.

An alternative treatment to that of the triangular net on the same mathematical results is to prepare a "slide rule" working on the principle indicated in Fig. 1. Its operation involves subjective alignment of two scales, which is complicated in practice by the size of the rule.

Practical comparison of performance of the two procedures (net and slide rule) was made on a series of results with several operators. The errors were examined statistically and showed no significant difference between the best performances of the two methods. Some operators, however, had significantly greater errors with the net than others, whereas the slide-rule operation showed a more consistent level of performance. A general preference for the slide rule was expressed, owing to the fatigue resulting from use of the net, which was of closer mesh than in the previous work[6] because of the accuracy required.
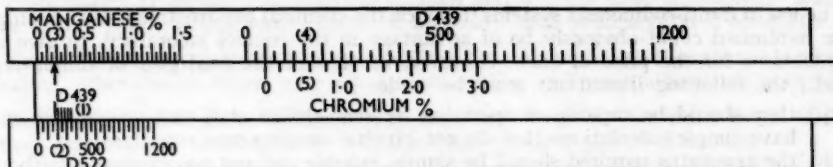

Fig. 1. Schematic diagram of slide rule

Slide rule prepared for solution of the equations—

Chromium, $\% = 3\cdot49D_{439} - 0\cdot657D_{522}$
Manganese, $\% = 1\cdot284D_{522} - 0\cdot0478D_{439}$

The density scales are multiplied by a factor of 1000 to eliminate the decimal point, *i.e.*, an optical density of $0\cdot10$ is read as 100.

To use, set $D439$ (scale 1) opposite $D522$ (scale 2) and read manganese $\%$ (scale 3) at the arrow; without moving the slide, read chromium $\%$ (scale 5) opposite $D439$ (scale 4)

If reproduction is not therefore a vital factor, it would seem preferable to use the slide-rule method of evaluation.

TERNARY SYSTEMS—

These have been only superficially examined from the standpoint of calculation, as the chemical complication of binary systems provided sufficient problems. There is no reason why the net system should not be applied to equations of more than two variables having solutions of the form—

$$[C_1] = k_1D_1 - k_2D_2 - k_3D_3$$
$$= k_1D_1 - (\underbrace{k_2D_2 + k_3D_3})$$
$$\text{triangle 1}$$

$$\underbrace{\qquad\qquad\qquad}_{\text{triangle 2}}$$

The slide-rule system would demand two slides, and it may well be that at this level the complication of extra parallel scales will confuse the issue to an extent that will render the slide rule less satisfactory than the net.

A word should be said here about a binary system involving a single reagent reacting with two ionic species, such as the system molybdenum - vanadium - catechol.[7] If both reactions should be reversible and achieve dynamic equilibria of the form—

$$A^+ + C' \rightleftharpoons AC,$$
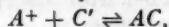
where AC is the coloured complex, A^+ the ion to be determined, and C' the reagent that similarly reacts with B^+, the analysis of the mixed colour will not be possible with two measurements, but will require a third optical-density measurement to define the concentration of unreacted reagent, and thus the calculation will be a ternary one.

ADAPTATION OF THE SPEKKER ABSORPTIOMETER FOR USE WITH INTERFERENCE FILTERS

General details of the Spekker photo-electric absorptiometer are so familiar that elaboration is not required. In view, however, of the requirements of precise optical-density measurement for composite procedure, because of the possible errors in differences, attention is drawn to the measuring diaphragm of the Spekker model H760. This design of a wear-free backlash-free cam with a long reading scale must contribute, in my opinion, to more satisfactory long-term reproducibility than the potentiometer transmission controls of the spectrophotometer.

As is well known, use of the mercury-vapour lamp with customary gelatin narrow-band filters gives monochromatic light of adequate purity to ensure linear calibration curves for concentration against optical density, which are essential for composite work. The choice of mercury lines is limited, however, and, when the tungsten-filament lamp is substituted, the polychromatism of the light passed by the filters may give rise to curvature of the calibration curves. A further limitation of the normal tungsten-filament lamp used is the low intensity, particularly at the blue end of the spectrum. The use of any narrow-band interference filters with this source would reduce the signal available from the photocell for accurate balancing. Hence, before such filters could be used, a lamp of higher intensity had to be introduced. The use of a more sensitive galvanometer is excluded by cost and lack of stability under severe working conditions.

It was found that a standard projector lamp was available (Ediswan S1/162) with identical filament height to the standard, but rated at 500 watts as opposed to 100 watts. Although this does not require forced-draught cooling to maintain the lamp efficiency, it was found that the lamphouse became overheated with the extra power involved. Accordingly, a forced draught was introduced to facilitate cooling. An air blower was fitted with a nozzle leading into the base of the instrument. Deflectors sent the air stream through the holes in the lamp bracket up into the lamphouse. The inner light shield was modified to take in part of the air stream to reduce the tendency of the lamp envelope to bulge during use.

The lamphouse could now operate for some hours without overheating, but, when the shutter was opened, the heat filters at the sides of the lamphouse cracked with the intense heat of the beam. A system of flow-through water cells fitting inside the lamphouse was therefore designed, and these adequately protected the glass optical system from heat without unduly reducing the intensity of the visible beam. It was realised that the introduction of the water cells approximately 1 cm deep with 1-mm glass faces would disturb the focus of the instrument slightly, but it did not apparently affect the accuracy of the readings.

G.A.B. INTERFERENCE FILTERS—

Two pairs of interference filters were purchased from Geraetebau-Anstalt Balzers (G.A.B.), Liechtenstein, and before they were used in the Spekker absorptiometer a general examination of their characteristics was made. Two procedures were used—

(a) By using a large stigmatic grating spectrograph,[8] the transmission of the filters to tungsten light was determined for the whole filter area. The normal arc stand was replaced by the 500-watt tungsten-filament lamp and the filter to be examined was placed next to the condensing lens, in order to combine light from different parts of the filter on to the slit.

Step spectrograms of equal duration were taken for the unfiltered light and that transmitted by the different filters. Exposures were also made for comparison with the copper d.c. arc by using a Hartmann diaphragm to establish the exact wavelength of peak transmission.

The step spectrograms were examined with a microphotometer to give transmission curves of the filters. The diaphragm exposures were measured to determine the position of peak density and the wavelength was assessed by interpolation between known arc lines.

(b) A Unicam SP600 spectrophotometer was used to examine the heterogeneity of the filter. With the wavelength set at the mean peak value determined in (a), the transmission at various positions across the filter along two perpendicular axes was measured. When a significant variation was shown in the transmission at different positions, the transmission - wavelength relationship was determined at selected extreme positions.

The results of these examinations are summarised in Table I. Filters 1 and 2 showed a few pinholes, but these were not a significant proportion of the total area as confirmed by the absence of any detectable shoulder or background to their transmission curves.

The filters are shown to be of high quality with notable sharp cut-off at the base of the transmission curves compared with those available from British sources. Some heterogeneity is shown, the importance of which will depend on the purpose for which they are

required. There is some divergence from the marked wavelength, which could prove serious if the filters were to be used for isolation of line spectra, *e.g.*, in flame photometry. Filters 3 and 4 were generally of poorer quality than 1 and 2, particularly in respect of surface variations, despite the absence of pinholes from these. The somewhat disturbing variations in transmission at the mean wavelength may not for some purposes be serious when this reflects a change in peak wavelength rather than a variation in total optical density across the filter.

TABLE I

Filter No.	Nominal peak, $m\mu$	Nominal band-width, $m\mu$	Over-all mean transmission determined by method (a)							Surface variations determined by method (b)	
			λ_{max}, $m\mu$	Maximum transmission, %	Bandwidths, $m\mu$*					Transmission at λ_{max} %	λ_{max}, $m\mu$
					1/2	1/5	1/10	1/20	1/50		
1	438	9	437	28	5	9	12	15	—	7% in one axis	436–437
2	439	6·5	439	30	5·5	9	12	15·5	—	negligible	—
3	521	12	516	33	10·5	16·5	21	25	33	≃ 7 to 10% in both axes	516–517
4	522	11	518	31	10·5	16·5	21	25	33	≃ 15% in both axis	Wide variations up to 6 $m\mu$

* Bandwidth is defined as the width of the transmission curve in $m\mu$ when the transmission is a specified fraction of maximum transmission.

PRACTICAL APPLICATION OF INTERFERENCE FILTERS IN THE SPEKKER ABSORPTIOMETER

It is intended to deal with the chemical results of a composite procedure in which these filters are used in later papers. The present discussion will cover their physical performance in view of the results outlined above.

The sensitivity of the modified Spekker absorptiometer with the 500-watt lamp and the G.A.B. filters in both sides of the instrument was measured. Solutions of various concentrations were prepared and their optical densities were determined relative to water by the zero setting method.[9] The right-hand drum was then set 0·01 optical-density unit (1 drum division) from the balance position and the deflection on the galvanometer was noted. The sensitivity can then be expressed as mm per drum division, with the following results—

Optical density	0·2	0·45	0·7	1·0
Sensitivity at 522 $m\mu$, mm per drum division	12	6	4	2
Sensitivity at 439 $m\mu$, mm per drum division	15	7	6	3

The galvanometer used was a standard Cambridge spot galvanometer normally supplied and the sensitivity control on the instrument was used at its maximum position.

A vital feature in filters for the absorptiometer is homogeneity in view of the method of measuring optical density. The accurately calibrated drum assumes perfectly even illumination over an area approximately $1·2 \text{ cm} \times 1 \text{ cm}$, followed by a filter uniform over a similar area. Lack of uniformity in the filter will cause errors in the optical-density measurement (for absorptiometers with photocell response for direct optical-density measurement this error would not arise).

In assessing the possible chemical errors that may arise, however, consideration must be given to the absorption curve of the species being determined. If the curve is smooth and relatively level at the point of measurement and any filter variations are of wavelength rather than total optical density, errors in the final chemical result will be small. If, however, the absorbent has a complex absorption curve, such as permanganate, wavelength deviations could be serious.

The modified Spekker absorptiometer was used with the right-hand filter being in turn either No. 3 or No. 4 in their four possible orientations. The left-hand filter was the remaining filter of the pair; the orientation of this filter is unimportant, as the left-hand side of the instrument is static for the two stages of reading. Indeed, it may well be that a simple gelatin filter will be adequate in future for reliable compensation of light-source fluctuation. Ten accurate standard solutions of oxidised potassium permanganate were measured with

each filter arrangement and the calibration graph of concentration against optical density was plotted.

The calibration graphs obtained all had deviations from linearity, some as large as 0·02 optical-density unit. It was found impossible, however, to relate these variations directly to those shown in the filters by the spectrophotometer. This may well be due to the complex nature of the permanganate, as already mentioned. In use, it has been found possible to select an optimum orientation of the filter and to evolve a correction graph or table. Time alone can prove the ageing characteristics of these filters, but it is to be hoped that such corrections will remain constant. In predicting ageing properties, an important difference from gelatin filters is that radiation that is not transmitted is reflected and not absorbed. Consequently, less energy is taken up by the filter and there is less likelihood of the nature of the filter being changed than with a gelatin filter, in which the chemical dye may dissociate after absorbing energy.

Conclusions

The work described makes possible practical consideration of composite spectrophotometric methods for the control laboratory, provided that the over-riding economics of such procedures are borne in mind. The problems of evaluation can be simplified, without resorting to calculating machines, by graphical means adapted for the particular problem. It is possible to convert the simple Spekker absorptiometer for use with interference filters so as to give complete freedom of choice for the wavelength of measurement. The interference filters examined have been found suitable provided their mode of use is standardised.

I thank Miss J. T. King-Cox, who assisted in the practical examination of the interference filters, and P. H. Scholes, Esq., B.I.S.R.A., for helpful interest and comments.

The work on graphical calculation was made possible by the tolerant co-operation of the staff of the I.N.O. (Sheffield) Drawing Office, who produced both net and "slide rule." They also assisted by designing the flow-through water cells for the absorptiometer lamphouse.

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Notes

DERIVATIVES OF 1-AMINO-2-NAPHTHOL-4-SULPHONIC ACID AS REAGENTS FOR THE COLORIMETRIC DETERMINATION OF ZINC

Commercially available dye-stuffs derived from 1-amino-2-naphthol-4-sulphonic acid have been examined as potential reagents for the colorimetric determination of zinc. One of these, chrome fast black CAT, is exceptionally sensitive for visual determinations. Methods of using chrome fast cyanine B (Clayton Dyestuffs Co. Ltd.; Colour Index No. 202), chrome fast black CAT (Clayton Dyestuffs Co. Ltd.; Colour Index No. 203) and Solochrome red ERS (Imperial Chemical Industries Ltd.; Colour Index No. 652) are described and the concentrations at which some common metals interfere are given.

The dye-stuff 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulphonic acid (Colour Index No. 203) has been recommended by various workers as an indicator for the titration of metals, especially magnesium and zinc, with sequestering agents.[1,2,3,4] This dye-stuff, together with the closely related 1-(1-hydroxy-2-naphthylazo)-2-naphthol-4-sulphonic acid [chrome fast cyanine G (Clayton Dyestuffs Co. Ltd.; Colour Index No. 201)], 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonic acid [chrome fast cyanine B (Clayton Dyestuffs Co. Ltd.; Colour Index No. 202)] and 1-(2-hydroxy-1-naphthylazo)-5-nitro-2-naphthol-4-sulphonic acid [Solochrome black A (Imperial Chemical Industries Ltd.; Colour Index No. 204)], have been found to be sensitive reagents

for the colorimetric determination of very small amounts of zinc. Although they are not specific for this element, the fact that they are simpler to use than dithizone[5,6] and more sensitive than the best of the styryl dye-stuffs[7,8] may make them valuable in some circumstances. The transmission curves of these dye-stuffs and their zinc complexes have been measured on a Beckman DU spectrophotometer. With each it was seen that the greatest difference between a blank and the zinc complex was at a wavelength at which the transmission of the blank had a low reading and that of the zinc complex a high reading. A more suitable reagent for use with the Spekker or similar type absorptiometer is 1-(5-hydroxy-3-methyl-1-phenylpyrazolylazo)-2-naphthol-4-sulphonic acid (Solochrome red ERS) the yellow colour of which is changed to a bright bluish red by zinc and so the absorption is higher when more zinc is present.

The most sensitive of these dye-stuffs for use with an absorptiometer are C.I.203 and C.I.652; they will each determine zinc at a concentration as low as 0.01 μg per ml when a cell having a 4-cm light path is used. C.I.202 is less sensitive and may conveniently be used for the determination of zinc at concentrations between 0.5 and 4.0 μg per ml. For visual determination in Nessler glasses, the most suitable dye-stuff is C.I.203 and a solution having a concentration of zinc as low as 1 part in 200,000,000 can be distinguished from a blank solution.

METHOD

The methods of using the most satisfactory of the dye-stuffs follow.

PROCEDURE—

(a) *Use of C.I.652 to determine 0.1 to 1.0 μg of Zn^{2+} per ml*—Put 1 ml of a 0.1 per cent. solution of C.I.652 in a 25-ml calibrated flask and add 1 ml of a 2.5 per cent. solution of anhydrous sodium carbonate. Add the solution containing the zinc and dilute to the mark. After 5 minutes take readings for the solution against a blank solution in a Spekker absorptiometer in 1-cm cells, using an Ilford No. 604 green filter.

(b) *Use of C.I.203 to determine 0.1 to 1.0 μg of Zn^{2+} per ml*—Put 0.75 ml of a 0.1 per cent. solution of C.I.203 in a 25-ml calibrated flask and add 1 ml of a 2.5 per cent. solution of anhydrous sodium carbonate. Add the solution containing the zinc and dilute to the mark. After 5 minutes take readings against a water blank in a Spekker absorptiometer in 1-cm cells, using an Ilford No. 608 red filter.

(c) *Use of C.I.202 to determine 0.5 to 4.0 μg of Zn^{2+} per ml*—Place 2.0 ml of a 0.1 per cent. solution of C.I.202 in a 25-ml calibrated flask and add 2 ml of a 2.5 per cent. solution of anhydrous sodium carbonate. Add the solution containing the zinc and dilute to the mark. Take readings against a water blank after 5 minutes in 1-cm cells, using an Ilford No. 608 red filter.

(d) *Use of C.I.652 to determine 0.01 to 0.1 μg of Zn^{2+} per ml*—Put 0.5 ml of a 0.02 per cent. solution of C.I.652 in a 25-ml calibrated flask and add 0.5 ml of a 0.5 per cent. solution of anhydrous sodium carbonate. Add the sample containing zinc and dilute to the mark. After 5 minutes take readings against water in 4-cm cells, using an Ilford No. 604 green filter.

(e) *Visual determination of 0.0025 to 0.01 μg of Zn^{2+} per ml*—Add 1.5 ml of a 0.02 per cent. solution of C.I.652 or 1 ml of 0.02 per cent. solution of C.I.203 to 1.5 ml of a 0.5 per cent. solution of anhydrous sodium carbonate in a 100-ml Nessler glass. Add the sample under test and make up to 100 ml. Stir well and set aside for 5 minutes before comparing the colour with those of standards. The relative shades of colour remain unchanged for several hours.

In all these tests the use of an excess of sodium carbonate solution over the amount specified does not spoil the results.

INTERFERING METALS

The amount of metal (in μg per ml) indicated in the following Table gives a colour approximately equal in shade and intensity to that given by 1 μg of zinc per ml—

	C.I.201	C.I.202	C.I.203	C.I.204	C.I.652
Mg^{2+}	2	3	3	4	6
Ca^{2+}	> 1000	200	30	200	> 1000
Ba^{2+}	> 1000	> 1000	> 1000	> 1000	> 1000
Sr^{2+}	> 1000	> 1000	> 1000	> 1000	> 1000
Cd^{2+}	1	4	4	2	3
Zr^{2+}	> 500	> 500	> 500	> 500	> 500
VO_2^{2+}	60	80	80	80	80
Co^{2+}	0·3	0·8	0·5	0·8	0·8
Ni^{2+}	1	1	1	1	0·6
Hg^{2+}	> 1000	> 1000	> 1000	> 1000	30

The following metals form dark colours or precipitates that mask or prevent the zinc colour reaction—

	C.I.201	C.I.202	C.I.203	C.I.204	C.I.652
Be^{2+}	250	250	250	250	250
Pb^{2+}	6	80	20	60	20
Ag^{+}	40	40	40	40	40
Fe^{3+}	20	20	20	20	20

It will thus be seen that very sensitive methods for the determination of zinc have been described; they may be of use under conditions in which interfering metals are absent.

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Apparatus

MODIFICATION TO APPARATUS FOR THE MICRO-DETERMINATION OF OXYGEN, NITROGEN AND HYDROGEN IN TITANIUM AND SOME OTHER METALS

IN a recent publication by Booth, Bryant and Parker,[1] an apparatus is referred to for the micro-determination of oxygen, nitrogen and hydrogen in titanium and some other metals. This apparatus is based on a design described by Gregory, Mapper and Woodward[2] and incorporates a "tree" for retaining samples before analysis.
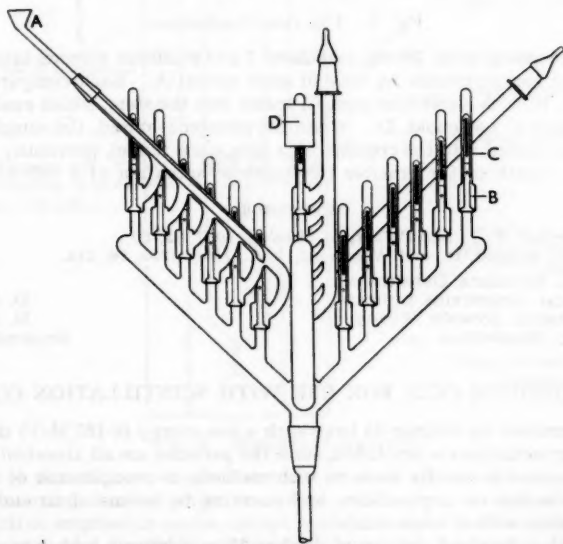

Fig. 1. Side view of apparatus

The detachable "tree" usually contains twenty-four cone and socket joints, which must be sealed with wax each time a batch of samples is examined. This is time-consuming and, unless the joints are cleaned regularly, leakage may be experienced.

An improved type of "tree," shown schematically in Figs. 1 and 2, has been designed and made in these laboratories. This modified component achieves the same analytical objective with only four cone and socket joints, thus minimising the possibility of leaks, and has the added advantage that it may be conveniently loaded *in situ* in about 5 minutes.
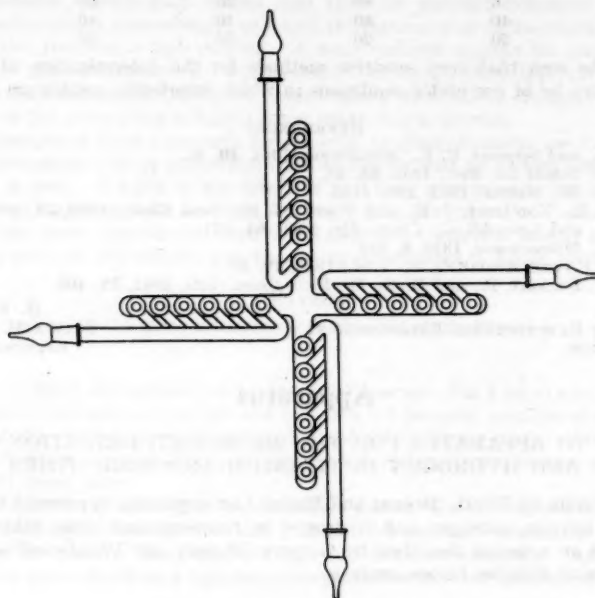
Fig. 2. Top view of apparatus

Samples, each weighing about 30 mg, and about 7 g of platinum wire are introduced separately into the twenty-four compartments by way of glass funnel A. Each compartment has a loose fitting glass plunger, B, with a soft-iron core, C, sealed into the stem, which enables it to be raised magnetically by means of a solenoid, D. When the plunger is raised, the sample is released from its compartment and guided into the crucible by a long silica funnel, previously lowered to within about 5 mm of the mouth of the crucible by magnetic actuation of a soft-iron counterweight.

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A FLOW-THROUGH CELL FOR USE WITH SCINTILLATION COUNTERS

THE beta particles emitted by sulphur-35 have such a low energy (0·167 MeV) that the use of the usual liquid-counting techniques is precluded, since the particles are all absorbed in the glass walls of the counter. Recourse is usually made to such methods as precipitation of the sulphur-35 as barium sulphate, collection on a planchette and counting by means of an end-window Geiger - Müller tube, preferably with a mica window.

During studies that involved the use of sulphur-35 as sulphuric acid, it was found desirable to avoid the use of solid counting. It was thought that scintillation counting techniques might offer a means of achieving this end, since a cell to hold liquid could be constructed from phosphorescent material, thus affording a means whereby the energy of the weak beta particles could be converted to light energy, which could be measured by means of a photomultiplier tube. A

cell was constructed of Pamelon (obtained from Isotope Development Ltd., Aldermaston, Berks.) and experiments were undertaken to determine the sensitivity of the method.

It soon became apparent that, although the method had sufficient sensitivity for the purpose, it was not without difficulties. It was necessary to orientate the cell on top of the photomultiplier tube, within the lead castle, in exactly the same position each time a sample was counted. Optical contact had to be made between the cell and the tube; this involved dispensing silicone oil in semi-darkness. The major difficulty was due to the Pamelon cell being light sensitive; that is, when exposed to light and replaced within the counter, the cell gave an abnormal background count, which slowly decayed after several hours, only to increase again on further exposure to light.

These difficulties were overcome by using the flow-through cell shown in Fig. 1. The cell can be placed in position within the lead castle and can be filled, emptied and washed without being removed from the counter. If necessary, the whole assembly can be dismantled quickly.
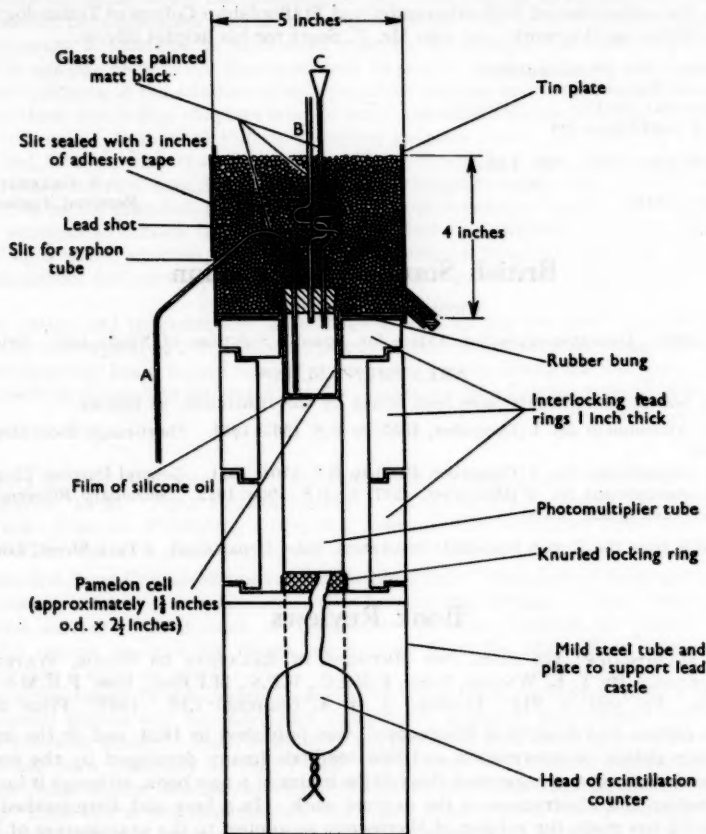

Fig. 1. Diagram of apparatus

In use, 40 ml of the radioactive solution to be counted are poured into the cell by way of funnel C. After counting, 5 ml of water are added, which cause a syphon to operate by way of tube A. The cell is emptied to waste, except for 1 or 2 ml. Wash solution is then admitted to the cell by way of funnel C and the sequence of operations is repeated until the background count is reduced to normal. Tube B is merely a pressure-balance tube.

The apparatus described has been found to be very convenient in use and with its aid linear relationships between counting rates and concentrations of sulphur-35 have been obtained. The results of a typical experiment are shown in Table I.

TABLE I

RELATIONSHIP BETWEEN COUNTING RATE AND CONCENTRATION OF SULPHUR-35

Sulphur-35 present, microcuries per 40 ml	Activity, counts per minute	Activity less background, counts per minute
0·000	165	—
0·375	843	678
0·750	1461	1296
1·125	2175	2010
1·500	2810	2645
1·875	3460	3295
2·250	4133	3968
2·625	4750	4585
3·000	5432	5267

I thank the authorities of Wolverhampton and Staffordshire College of Technology, who provided the facilities for this work, and also Mr. F. Scott for his helpful advice.

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NEW SPECIFICATIONS*

B.S. 975: 1957.   Density-composition Tables for Aqueous Solutions of Nitric Acid.   Price 12s. 6d.

AMENDMENT SLIPS*

PRINTED slips bearing amendments have been issued by the Institution, as follows—

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    PD 2932—Amendment No. 1 (December, 1957) to B.S. 1704: 1951.   General Purpose Thermometers.

    PD 2933—Amendment No. 3 (December, 1957) to B.S. 1900: 1952.   Secondary Reference Thermometers (Centigrade Scale).

    * Obtainable from the British Standards Institution, Sales Department, 2 Park Street, London, W.1.

Book Reviews

ANALYTICAL MICROSCOPY: ITS AIMS AND METHODS IN RELATION TO FOODS, WATER, SPICES AND DRUGS. By T. E. WALLIS, D.Sc., F.R.I.C., F.P.S., M.I.Biol., Hon. F.R.M.S. Second Edition. Pp. viii + 215. London: J. & A. Churchill Ltd. 1957. Price 25s.

The first edition of "Analytical Microscopy" was published in 1923, and in the intervening years the accumulation of information and new methods (many developed by the author) has necessitated such extensive revision that this edition is almost a new book, although it incorporates the subject matter and illustrations of the original work. In a long and distinguished scientific career Dr. Wallis has made the subject of Microscopy as applied to the examination of Vegetable Drugs, Foods and Water Deposits peculiarly his own, and in this book he gives a practical exposition of a valuable adjuvant to Food and Drug Analysis.

The treatment is practical throughout, most of the chapter headings referring to particular procedures, which are first described, and their application is then exemplified by reference to the examination of particular objects or commodities. Thus after an Introduction, the second chapter is headed Simple Methods of Preliminary Treatment and includes instructions for the examination of seeds and fruits and gives 77 diagrams of varieties, many being those of weeds liable to occur in agricultural produce. The same chapter also embraces descriptions of infesting insects as well as covering an·account of powdered lucerne. Particularly valuable to the food analyst is the third chapter entitled Surface Preparations and Sections, because it is mainly devoted to copiously

illustrated descriptions of the culinary herbs and their common adulterants.   Here we have fine drawings of the macroscopical and microscopical characters of important commodities, notably mint and sage, and also of adulterants such as ailanthus, mulberry, phlomis and cistus.   The following chapter, designated Sedimentation and Centrifugation, is concerned with deposits found in waters, including diatoms, algae, fungi, protozoa, water fleas, rotifers, moth scales, worms, mites and insects, all finely illustrated.   So the book goes on, giving accounts of the microscopy of commercial starches, cereals, honey, infesting mites of flour and fodder, all complete with diagrams.   In a chapter entitled Micromorphology allusion is made to the author's discovery that traces of dissolved silica influence the crystalline structure of the scale that is formed when natural waters are boiled.   A more complete account of this phenomenon was recently given by Dr. Wallis in his Presidential Address to The Royal Microscopical Society and has now been published (March, 1957) in that Society's *Journal*.

Although the book covers the examination of a large number of commodities, and especially foods, it should be emphasised that no attempt has been made in it to provide a comprehensive atlas of drawings to illustrate all substances requiring microscopical examination for their assessment.   The aim has been to tell the reader how to prepare material for microscopical observation and to offer guidance in the selection of clearing and mounting agents and in methods of manipulation.   The three concluding chapters treat of more specialised Microscopy and deal with Measurement and Drawing, Numerical Values, including palisade ratios, the stomatal index, vein islet numbers and, lastly, a chapter on Quantitative Microscopical Analysis.   There are two appendixes, the one giving numerical data, the other formulae for reagents mentioned in the text, and the book closes with a useful classified bibliography and a comprehensive index.

One ventures to remark that the value of the last two chapters would have been enhanced by including a wider selection of references to the original scientific literature.   Modesty on the part of the author doubtless has something to do with this omission, since much of the work is his own.

Both author and publisher are to be congratulated on the fine production of this handsome volume, which is offered at a very modest price.   I understand that the preparation of the manuscript and drawings has occupied most of the author's leisure during the last 6 years; many fellow scientists will have cause to be grateful to Dr. Wallis for spending his time so generously to their profit.   N. L. ALLPORT

SPOT TESTS IN ORGANIC ANALYSIS. By FRITZ FEIGL, Eng., D.Sc.   Translated by RALPH E. OESPER, Ph.D.   Fifth English Edition.   Pp. xx + 616.   Amsterdam, London and New York: Elsevier Publishing Company; London: Cleaver-Hume Press Ltd.   1956.   Price $10.00; 55s.

In the first three English editions of Feigl's "Spot Tests" the application of spot tests to organic analysis was included as a comparatively small, but growing, section.   Three years ago the increase of material warranted the division of "Spot Tests" into two volumes, the second of which dealt solely with organic analysis (for review see *Analyst*, 1954, **79**, 722).   This volume has now been expanded into a separate work.

The arrangement of the contents—survey of the subject, technique, preliminary tests, tests for functional groups and for individual compounds, technical applications—remains the same as in the previous edition.   Much of the text has, however, been rewritten, and the number of tests reported has been increased by nearly half.   As before, full practical details are given of each test, with limits of identification, known interferences and, when possible, the reactions underlying the test.   Each test is well documented, and a new chapter gives nearly a hundred references to other general studies of organic spot tests.   The translation is a model of clarity, and there is an admirably detailed subject index.

The expansion of the book in such a short time is a measure of the increase of information on spot tests applied to organic compounds.   Much of this has come from Professor Feigl and his coworkers, but, if the subject arouses the same interest in other workers as inorganic applications of spot tests did, we can expect a much greater increase in the future.   This is highly likely.   It is pointed out in the book how much remains to be done in the way of improving tests, of adapting known reactions as spot tests and of finding new tests.   Workers who are attracted to this field will have cause to be grateful to Professor Feigl for the groundwork he has done.   Analysts will, in the meantime, find in the book much useful practical information that will affect classical organic analysis as well as the particular field of spot tests.   DAVID W. WILSON

MATHEMATICS AND STATISTICS FOR USE IN PHARMACY, BIOLOGY AND CHEMISTRY. By L. SAUNDERS and R. FLEMING. Pp. x + 257. London: The Pharmaceutical Press. 1957. Price 27s. 6d.

The authors have undertaken the task of attempting to remedy the deficiencies in mathematical and statistical knowledge and understanding often encountered in students and graduates of pharmacy, biology and allied branches of science.

In general, the mathematical chapters of the book follow the conventional pattern and justifiably, in view of the readers for whom they are intended, dispense with the niceties of mathematical rigour, appealing more to the reader's intuition and intelligence.

Unfortunately, however, the conventional approach adopted perpetuates the lack of balance in mathematical material that is too often found in books intended for such readers, particularly at the expense of practical computation methods. Thus a whole chapter is devoted to the little used topic of trigonometry, whereas the very important subject of simultaneous linear equations is relegated to a two-page appendix on determinants. Similarly the fitting of equations to experimental results is dealt with in a chapter of only seven pages, without any indication even of the existence of simple numerical methods for curve-fitting. Deficiencies in the treatment of computational methods are also evidenced by the lack of any discussion of interpolation, of the solution of simple non-linear equations by successive approximation and of elementary numerical integration and differentiation.

The treatment of series is marred by several inaccuracies. For example, on p. 40, the ridiculous statement is made that the partial sums of a convergent series never exceed their limit. This is unfortunately almost immediately followed on p. 42 by the series $\pi = 4(1 - \frac{1}{3} + \frac{1}{5} - \frac{1}{7} \ldots)$, which is anyhow only conditionally convergent and, if summed in the order given, would yield partial sums alternately greater and smaller than their limit. Insufficient warning is given that power series have their limitations, and indeed on p. 84 the dangerous statement is made that any function can be so represented.

The statistical chapters are moderately successful in the treatment of probability and are well supplied with useful practical examples. The object of randomisation and experimental design, so important in biology and biological assay, is, however, never clearly explained or even stated. Such discussion as does appear is more likely to confuse than help. Thus, for example, on p. 169 it is contended that randomisation can be ensured by using a Latin square. This statement is immediately followed by a Latin square, obviously systematic in layout, and later on p. 173 by a 4×6 table of results, claimed to be a Latin square and analysed as if no design had been employed.

Sometimes generality of method is claimed or supplied when no such generality exists. In addition to the alleged generality of the power series already discussed is, for example, the claim on p. 175 that the underlying normal tolerance distribution is assumed in the interpretation of all quantal assays. Similarly on p. 13 no warning is given that dimensional analysis generally leads to undetermined functions rather than constants; incidently the example given would be such an instance, but for the non-dimensional assumption of dependence on inverse tube length.

As the symbolism of mathematics is one of the main hurdles the non-mathematical practical reader has to overcome, a list of symbols would have been helpful particularly, as near-synonyms (e.g., Σ and S for summation and a Gothic p, p and P for probability) are often employed.

On the whole the book is rather patchy in quality and would probably have been more successful if a less ambitious coverage had been attempted. The lack of practical numerical methods is likely to mean that, even though readers may learn to formulate their problems in mathematical terms, they will be ill equipped to solve them practically.   J. P. R. TOOTILL

MODERN CEREAL CHEMISTRY. By D. W. KENT-JONES, Ph.D., B.Sc., F.R.I.C., and A. J. AMOS, Ph.D., B.Sc., F.R.I.C. Fifth Edition. Pp. x + 817. Liverpool: The Northern Publishing Co. Ltd. 1957. Price 105s.; $15.25.

Cereals furnish staple foods for the inhabitants of all parts of the world and contribute substantial items to the diet of domestic animals and poultry. In consequence they and their products have come under the critical eye of all concerned with nutrition, and the resulting picture—sometimes white and sometimes brown—has not always been free from distortion. It is therefore important that the latest information should be readily available so that what is seen may accord with the facts. "Modern Cereal Chemistry" sets out to supply this information, and previous editions have appeared at approximately ten-year intervals, each of wider scope than its predecessor and adequately justifying the term "modern."

The general arrangement of this new edition is substantially the same as that of the last, which became so familiar to all food chemists and which was recognised as the standard work on the

subject.   The old chapter on Some Physico-Chemical Aspects of Flour has been deleted—parts being incorporated elsewhere—and a new one included on Infestation by Insects and Mites. Additional material appears in every chapter, and as a whole the increase is approximately 25 per cent.

During the decade since the last edition much important work has been published, and this has now been incorporated with critical appraisals.   One is conscious that the long practical experience of the authors has been brought to bear on their comments.

No better summing-up of this book can be given than by saying that the dust-cover is fully justified in claiming that "this new edition is probably the most comprehensive book on the subject and one which no modern cereal chemist should be without.   Covering the wide subject so completely it is invaluable also to the miller, the baker, and the many others whose work deals with cereals, and indeed to all those concerned in food technology."   J. R. NICHOLLS

QUANTITATIVE INORGANIC ANALYSIS: A LABORATORY MANUAL.   By R. BELCHER, D.Sc., Ph.D., F.R.I.C., F.Inst.F., and A. J. NUTTEN, B.Sc., Ph.D., F.R.I.C.   Pp. viii + 337.   London: Butterworths Scientific Publications.   1955.   Price 25s.

The authors have written a book that is designed primarily as a practical course for teaching quantitative inorganic analysis in Universities and Technical Colleges.

The main sections deal with laboratory apparatus and technique, gravimetric, titrimetric and colorimetric analysis, and a few applied analyses.   As might be expected, the range of determinations in all sections is limited, there being no inclusion in the gravimetric section, for example, of determinations of the less-common elements.   Here the authors are wise, as there is never time for such analyses in the ordinary college course and the better-known elements and radicles can provide ample opportunity for the beginner to gain experience.

Minor consideration is given to the so-called physical methods of analysis in spite of their importance in industry today, but the authors are right in maintaining, as they do in their preface, that in a University course classical analysis must always predominate.

The practical instructions provided for the various determinations are supported by an adequate amount of general theory, by notes on points of special practical importance, and by a selected number of references, but a detailed physico-chemical treatment is left to the lecture course or to the student's own study of T. B. Smith's well-known text-book.   In the gravimetric section of this present book, determinations other than those dealt with are often mentioned. This information, although of interest, is more suitable for a text-book than for a laboratory manual such as this purports to be.   In its place, I would have preferred to see an adequate treatment of the effect of variations in temperature on the measurement of volumetric solutions, a subject that receives only incidental mention.

Much useful instruction is supplied for the student, but there are many points on which I disagree with the authors.   When aperiodic balances are not available, the method of swings should, in my opinion, always be insisted upon and not the method of moving the rider along the 0·1-mg notches until deflections coincide; before being weighed, weighing bottles should never be handled by bare fingers, and the weighing-out of an amount of substance required for an exactly decinormal solution should be discouraged.   Neither have I found it necessary to invert a stoppered calibrated flask, filled to its mark, thirty to forty times to ensure thorough mixing of the contents (p. 141).   The preparation of constant-boiling hydrochloric acid is not particularly troublesome (p. 157); indeed, it is an excellent method for preparing standard acid and one well within the capacity of a second-year student.   A curious omission in the text is that no mention is made of the need for rinsing burettes and transfer pipettes with the solution to be used before a measurement is carried out.

Many points in the text will commend themselves to the reader.   The short chapter on desiccators emphasises the difficulties associated with the proper use of desiccants, but, as specified cooling times are seldom laid down, the student may find it difficult to know when to remove his crucible "as soon as it is cool," or, p. 53, to "weigh to constant weight, when it has cooled to the temperature of the balance."   The inclusion of a description of the Hartley funnel, an improved type of Buchner funnel that deserves to be better known and more widely used than it is at present, is a good feature.   So is the direction of the reader's attention to the appreciable solubility of the nickel - dimethylglyoxime complex in the hot mother liquid and the need for cooling before the filtration is carried out.   The description of the silver reductor for determining iron is a welcome inclusion in a text of this kind, but the instruction to use a glass tube of the same dimensions as those of the Jones reductor nullifies one of its advantages over the latter.   I agree with the authors'

considered opinion "that adsorption indicators have been somewhat overrated" and "only very few give good end-points." Students have little success in using many of these indicators.

Some of the statements in the text are open to question: thus on p. 94 we are told to "Dissolve the residue remaining in the beaker in the minimum volume of hot distilled water and transfer it quantitatively to the filter collecting the filtrate in a beaker"; that solid ferrous ammonium sulphate is stable (p. 206); that the precipitate obtained with ferric ions and N-benzoylphenylhydroxylamine must be ignited to ferric oxide (*cf.* Shome, *Analyst*, 1950, **75**, 27); that $MgHPO_4$ does not go to the pyrophosphate on ignition (p. 77); that the ferric iron - cupferron complex may be weighed after drying at a suitable temperature (p. 70); and finally, that felspar should be heated to 250° C for 1 hour before a determination of the alkalies in it is made (p. 316).

Typographical mistakes are few in number, but the formulae given for uranyl and zinc acetates on p. 88 are wrong; the one-hole rubber bung of the text on p. 167 has two holes shown in the diagram on p. 168, and the $24(NH_4)_2MoO_4$ of the equation on p. 174 should be $12(NH_4)_2MoO_4$. The figures relating to the equivalent weights of certain substances might well be checked by re-calculation, for they do not always agree with those calculated from the 1952 atomic weights given in the appendix. In the description of the determination of the alkalies in felspar a paragraph seems to be out of its order in the text, and the Kalignost solution to be added is not described; presumably it is the reagent described on p. 96. In order to complete the determination, reference must be made to p. 96 and not to the p. 90 indicated.

Fifty-four review questions are provided after the text, whereby the student can test his knowledge of the subject. One wonders what his answer will be to the question "How many methods, based on the method of completion, do you know for the determination of iron?"

The book will be of interest more to the teacher of analytical chemistry than to the practising analyst, to whom, I imagine, it will not have a wide appeal.

It is a reflection on the times and on present-day teaching that these authors, in urging the student-reader to present his experimental results in such a way that they can be assimilated at a glance, can tell him candidly the melancholy truth when they write "It should be borne in mind that the supervisor rarely has time to read carefully through the notebook. . . ."

L. S. THEOBALD

Publications Received

DENTAL PRACTITIONERS' FORMULARY 1957. Pp. 49. London: The British Medical Association *and* The Pharmaceutical Press. 1957. Price 3s.

FLAME PHOTOMETRY. By F. BURRIEL-MARTÍ and J. RAMÍREZ-MUÑOZ. Pp. xii + 531. Amsterdam: Elsevier Publishing Co.; London: Cleaver-Hume Press Ltd.; New York: D. Van Nostrand Co. Inc. 1957. Price 65s.

ORGANISCHE FÄLLUNGSMITTEL IN DER QUANTITATIVEN ANALYSE. By Dr. WILHELM PRODINGER. Fourth Edition. Pp. xvi + 246. Stuttgart: Ferdinand Enke Verlag. 1957. Price (paper) DM 33; (cloth boards) DM 35.60.

RECOMMENDED METHODS FOR THE ANALYSIS OF TRADE EFFLUENTS

REPRINTS of the Recommended Methods prepared by the Joint A.B.C.M. - S.A.C. Committee on Methods for the Analysis of Trade Effluents are now available from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1; price to members 1s. 6d., or to non-members 2s. 6d., each. Remittances made out to the Society for Analytical Chemistry must accompany orders, and these reprints are not available through Trade Agents.

Reprints Nos. 1 to 10 were listed last November. The following additional reprints are now available—

Reprint No. 11. Determination of Oxygen Demand (October, 1957).
Reprint No. 12. Determination of Antimony, Barium Soluble in Dilute Hydrochloric Acid and Cadmium (November, 1957).
Reprint No. 13. Determination of Synthetic Detergents (December, 1957).

Erratum

DECEMBER (1957) ISSUE, p. 813, 3rd line from foot of page. *For* "17 ml" *read* "170 ml".